Assessment of Permeable Reactive Barriers for Sulphate Reduction at the Former Steep Rock Iron Mine Site, Atikokan, Ontario.

by

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ABSTRACT

This study assessed if a permeable reactive barrier (PRB) could be used to reduce sulphate and metal concentrations of Hogarth pit lake, a sulphate-toxic (up to 2,000 mg/L) pit lake at the former Steep Rock iron mine site in Atikokan, Ontario. Both batch reactor and flow-through reactor experiments were performed to simulate a PRB at the bench-scale in order to assess the sulphate reducing capacity of different types of organic matter.

Batch reactor experiments were run using three different treatments to promote bacterial sulphate reduction in order to lower sulphate concentrations in water from the pit lake. Treatment 1 contained organic matter, creek sediment (sulphate reducing bacteria source), carbonate rock (acid neutralizing agent) and glacial till (non-reactive medium). Treatments 2 and 3 were similar to treatment 1, except that treatment 2 did not include creek sediment and treatment 3 contained molasses as a nutrient. Treatment 1 with horse manure and wood chips as the organic source resulted in >99% reduction in sulphate concentration, combined with increases in pH and bicarbonate levels, reduced redox and decreased metal concentrations. Bacterial sulphate reduction was also initiated with Treatment 2, although did not occur as quickly as treatment 1. The results of treatment 3 with molasses showed that no sulphate reduction occurred in the batch reactors. Based on these results, treatment 1 was selected for the flow-through experiment to simulate a PRB at a laboratory scale.

Flow-through reactor columns were run in duplicate and filled to create different reaction chambers that contained mixtures of treatment 1. The most effective sulphate-reducing flow-through reactors consisted of two reaction chambers separated by silica sand, which resulted in an overall sulphate reduction average of 46 % and 49 %. In comparison, all other flow-through reactors achieved a 39% reduction in sulphate concentrations. Sulphate reducing bacteria activity was evident after three weeks with reductions in redox values and sulphate concentrations and

increases in bicarbonate and pH levels. Results of flow-through reactor 1, reduced sulphate concentrations to <300 mg/L between weeks 3 and 5, and had a gradual increase for the remainder of the experiment to around 1000 mg/L. Results of flow through reactor 5, showed a decrease in sulphate concentration to <700 mg/L between weeks 3 and 8 before also increasing to around 1000 mg/L for the rest of the experiment. All other reactors generally decreased to 900-1000 mg/L after 2 weeks and remained around 1000 mg/L between weeks 3 and 20.

Sulphate concentration in water from the adjacent Caland pit lake, has a sulphate concentration of <300 mg/L, and a previous study at the site concluded that Caland pit water can be treated by a wetland ecosystem. Therefore, it is reasonable to conclude that a treatment system which consisted of a PRB flowing into a constructed wetland has the potential to reduce elevated sulphate levels in Hogarth pit lake. However, the flow-through experiments show that the residence time is a limiting factor in the life span of a PRB. Also, it is possible that sulphide precipitation is limited by the availability of divalent metals, in particular Fe^{2+}.

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CHAPTER 1: INTRODUCTION

1.1 Issues Regarding Pit Lakes

Pit lakes result after the closure of open-pit or surface mining operations, where water from surface runoff, precipitation and groundwater influx fill the pits. Pit lakes are characterized by a much higher depth to surface area ratio than natural lakes and cause them to become stratified. The chemical characteristics of the lake water can vary greatly with depth. High levels of acid, sulphate, and dissolved metals typify the water in many pits and result from oxidation of sulphidic waste rocks as well as interactions within pit wall rocks (Castro and Moore, 2000). Oxidation occurs when the sulphide minerals come into contact with dissolved atmospheric and/or dissolved O_2. These reactions release Fe(II), SO_4^{2-}, and acidity, and form acid mine drainage (AMD, Malmstrom et al., 2006). Pyrite is generally the most common sulphide in mine waste material and is readily oxidized with ferric iron to form sulphate and ferrous iron. The oxidation of iron sulphide can be expressed as:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 4SO_4^{2-} + 2Fe^{2+} + 4H^+$$

Ferric iron is subsequently regenerated by the bacterial oxidation of ferrous iron with oxygen (Boon and Heijnen, 1997; Christensen et al., 1996). As AMD reacts with atmospheric O_2, the oxidation of Fe (II) to Fe (III) results in a decrease in pH (Benner et al., 1999, 2002).

Treatment of AMD requires altering the redox environment and the pH of the mine water in order to limit the solubility of unwanted water components and improve the water quality (Blowes et al., 2003). AMD water can contain aqueous ions that may be toxic to humans or aquatic organisms. Treatment of AMD may be accomplished either by passive or active strategies.

Active treatment systems usually involve adding an alkaline reagent such as lime, or ammonia to the AMD, to increase pH and decrease the acidity of the AMD while also allowing the precipitation of metals, such as iron and nickel (Skousen and Ziemkiewicz, 2005). Lime treatment has been widely used throughout the last few decades because it is relatively simple, and it produces a predictable water quality (De Vegt et al., 1998). However, active treatments do have higher costs and are more labour intensive.

Alternatively, passive treatment has been defined as "the deliberate improvement of water quality using only naturally-available energy sources (i.e., gravity, microbial metabolic energy, photosynthesis), in systems which require only infrequent maintenance in order to operate effectively over the entire system design life" (page 335, Walton-Day, 2003). Since passive treatments offer a low cost and low maintenance alternative to active systems, research and experimentation into passive systems for use in the mining industry has increased in recent years.

A commonly implemented passive treatment, anoxic limestone drains (ALD) have proven to be effective for raising the pH and alkalinity of acidic mine water. ALDs typically consist of crushed limestone that is placed in a buried bed to intercept acidic water before it can react with atmospheric O_2 (Cravotta, 2003). Similarly, the addition of other alkaline substances, such as fly ash (e.g., Wang et al., 2006), to wastes rich in sulphide can prevent AMD. The presence of fly ash helps to neutralize acidic water, decreases metal solubility and can retain metals in solution by precipitation (Perez-Lopez et al., 2007). Also, the use of constructed wetlands, (e.g., Mitsch and Wise, 1998; Weider, 1992) have been used as a low-cost, low maintenance alternative to treat acid drainage. The plant species within engineered wetlands absorb metals which can be removed from the site at a later date (Mays and Edwards, 2001).

Another treatment for AMD is the installation of a permeable reactive barrier. The barrier is designed to remove metals and generate alkalinity by promoting sulphate reduction and metal sulphide precipitation (Benner et al., 1997; 1999). They may be relatively simple in design and consist of a dugout channel that is packed with reactive material and covered with a fine-grained soil to prevent infiltration of oxygen. The barriers are designed to intersect the path of migrating contaminated groundwater by excavating the aquifer material and replacing it with a reactive mixture (Golab et al., 2006). PRBs have generated a lot of interest in the remediation of subsurface contaminants because of their cost/benefit ratio versus traditional active remediation techniques. Once a PRB system is installed, it should have minimal maintenance costs for at least five to ten years (U.S. E.P.A., 1998).

Organic carbon can be used as the reactive material to support the reduction of sulphate and the removal of divalent metals contained in AMD by sulphate reducing bacteria (SRB). As organic matter within the barrier decomposes, it creates a zone of low redox potential, which promotes the growth of SRB. The bacteria obtain energy and nutrient sources by oxidizing the organic compounds and using sulphur as an external electron acceptor (Herbert et al., 1998). Sulphate reducing bacteria must meet specific environmental requirements in order for sulphate reduction to occur. The environment must be anaerobic with a pH greater than 5, although a study by Elliot et al. (1998) concluded that SRB were capable of sulphate reduction at pH values as low as 3.25. The environment must also have an appropriate organic substrate to be reduced, and material where the bacteria can be grown must be present (Dvorak et al., 1992; Gilbert et al., 2002). The bacteria require an anoxic and reduced microenvironment with a redox potential lower than -100 mV for optimal performance (Gilbert et al., 2004; Malmstrom et al., 2006). Under the right conditions, SRB capitalize on the oxidation of organic carbon and reduce sulphate to sulphide. This reduction can be expressed by the simplified reaction:

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3$$

The reduction of sulphate in the presence of an organic carbon (CH_2O) produces hydrogen sulphide (H_2S), releases bicarbonate (HCO_3^-), and results in an increase in pH and alkalinity (Blowes et al., 2003). Providing the availability of metal cations, the rise in dissolved H_2S concentrations increases metal sulphide precipitation as metal sulphides:

$$Me^{2+} + S^{2-} \rightarrow MeS$$

where Me represents a divalent metal such as Cd, Fe, Ni, Cu, Co, or Zn. The PRB is designed in order to establish the conditions that promote bacterial sulphate reduction and metal sulphide precipitation. Accumulation of metal sulphides would require periodically replacing the SRB media, while the spent material may have the potential to be reprocessed and the metals recovered (Kolmer and Johnson, 2001). The organic mixture within the barrier provides dissolved C, N, and P, and the water entering the barrier is generally high in sulphate, iron and other metals, which are essential for the growth and reproduction of the bacteria (Waybrant et al., 2002). Sulphide concentrations are controlled by the amount of sulphide produced from sulphate reduction minus the amount of sulphide removed through metal precipitation (Amos et al., 2004). Sulphate reducing activity in PRBs can be confirmed by lower sulphate concentrations and a lower redox potential (Neculita et al., 2007).

Laboratory and pilot scale tests of bioreactors have proven that sulphate reduction is effective at raising pH and removing sulphate and metals from mine water. One study showed an increase in pH from between 5.5-5.9 to 6.0-7.0, and a sulphate decrease of 82% (Waybrant et al., 2002). Column experiments by Tsukamoto et al. (2004) found an average 42% sulphate reduction. Also, a full-scale PRB installation at the Nickel Rim mine site (Sudbury, ON) had a 30% overall sulphate reduction over a 3 year period (Benner et al., 2002).

1.2 Experimental Methods

Batch reactor experiments were performed with different reactive media in order to determine their capacity to initiate sulphate reduction and lower sulphate and dissolved metals in the pit water. The results of the batch experiments were subsequently used to determine which treatment would be most suitable for use in a flow-through reactor, which simulate the properties of a permeable reactive barrier at the bench scale. Batch and flow-through reactor experiments were performed under conditions that simulate the typical environment in which sulphate reduction and metal sulphide precipitation should occur.

In order to establish conditions for the growth of sulphate-reducing bacteria, the reactive media needs to consist of an organic source, a bacterial source, a neutralizing agent, and a non-reactive porous medium (Waybrant et al., 1998, 2002). The organic sources need to be rich in organic carbon and considered to be potentially suitable to ensure bacterial sulphate reduction as well as be economically practical. A bacterial source can be obtained from the anoxic zone of a local creek. Limestone can be used as a suitable acid-neutralizing agent to generate sufficient alkalinity and quartz sand can be used as an inert material that ensures permeability within the reactor or barrier (Gilbert et al., 2004).

Batch reactor experiments are static (i.e., no water flows through the reactive media) thus reaction times are naturally larger and the water – reactive media ratio may not be representative of a laboratory- or field-based PRB. Consequently, it is hypothesized that the batch experiment will represent the maximum efficiency of the various reactive media. The batch experiments conducted for this project used locally available materials in order to minimize the costs that would be incurred in the construction of a full-scale barrier on the Steep Rock site.

The organic matter used in this experiment included: cow manure, composted straw, horse manure, wood chips and peat. The horse manure, cow manure and composted straw were obtained from a farm in Oliver-Paipoonge Township, near Thunder Bay, ON. Wood chips were acquired from a local pulp and paper mill (Abitibi-Bowater) and were a mixture of softwood and hardwood. The peat was obtained from a large peat bog near Dryden, Ontario and had been air dried prior to use.

Glacial till, used as a non-reactive medium, was taken from a gravel pit approximately 10 km along Boreal Road in Marks Township, near Thunder Bay, ON. Till was sieved to 1.00 - 2.00 mm. A mixture of calcite- and dolomite-bearing rock was obtained from the Steep Rock site, taken from the Mosher Carbonate formation. The rock was crushed and sieved to between 0.5 and 1.00 mm, and was used as the carbonate source to act as an acid neutralizing material. Creek sediment was from the anoxic zone of the McIntyre River at Lakehead University, Thunder Bay ON, approximately 10 cm below the surface of the riverbed. This material was black in colour and had a strong H_2S odour. Molasses (Crosby's Family brand cooking molasses) was bought from a local supermarket and used as a nutrient to enhance bacterial sulphate reduction in some of the experiments.

1.3 Site Description

The Steep Rock mine site is located ~5km north of Atikokan, Ontario, which is approximately 200 km west of Thunder Bay, Ontario (Fig. 1.1). Iron ore was discovered in 1930, and at the time was the richest deposit of iron ore in North America. However, the deposit was located beneath Steep Rock Lake and a massive engineering project was required in order to open pit and underground mine the ore. First, two major diversions of the Seine River system were required. The construction of dams and diversion of this river began in 1943 and by the end of the year, pumping of the lake began. The diversion project resulted in only the West Arm of Steep Rock Lake being left intact, as the ore was beneath the middle and eastern arms of the original lake (Fig. 1.2). Secondly, approximately 570 billion litres of water and 225 million m^3

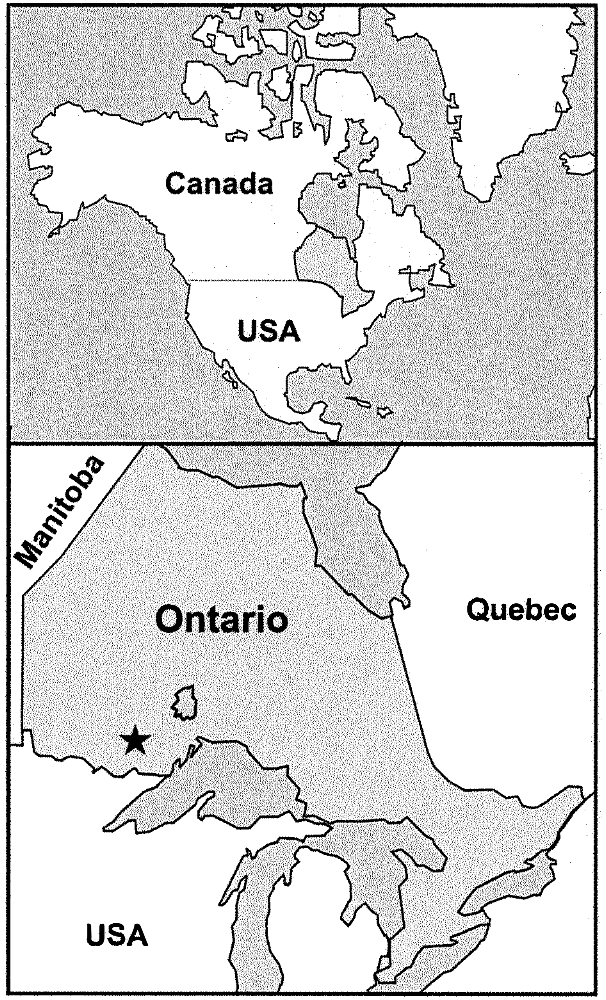


Figure 1.1: Map showing location of Atikokan, ON, represented by black star (from Conly, et al., 2008).

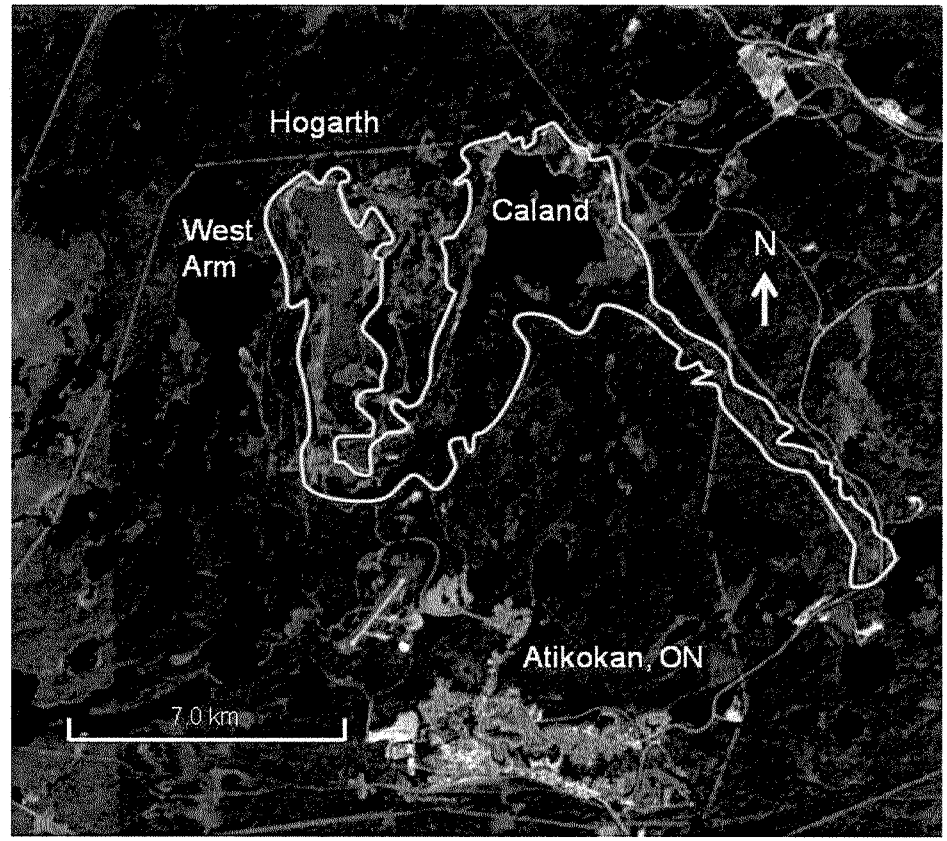


Figure 1.2: Map showing location of West Arm Lake and Hogarth and Caland pit lakes. Yellow outline represents the lake at original level prior to mine activity (base map from Google Earth; lake outline from Conly, et al., 2008).

of overburden were removed from the middle and eastern arm in order to reach the ore (Steep Rock Mines, 1943). Mining commenced in 1944, with the ore being extracted from four open pits (Hogarth, South Roberts, Errington and Caland) until 1979. Upon closure, approximately 200 acres of waste dumps were left in the area (Capper, 1978) and the open pits were left to be filled through combinations of groundwater, runoff and precipitation, creating four pit lakes, Hogarth, Caland, South Roberts and Errington. In 2004, Hogarth and South Roberts joined and are known as Hogarth Lake (Fig. 1.2). These lakes have been slowly rising each year and current water depths are slightly in excess of 200 m. Eventually the pit lakes will attain water levels equal to the original Steep Rock Lake, which is estimated to occur around 2066 (L. Mikkelsen, per. comm. 2011), and outflow from the combined Hogarth-Erringtion-Caland pit lake into the West Arm will occur.

Between 1998 and 2010 researchers at Lakehead University have seasonally monitored the physical and chemical water parameters at Hogarth and Caland pit lakes. Despite these lakes being in close proximity to one another (< 1km) and having similar geology, there are distinct differences in terms of the water chemistry and quality between the two pit lakes (McNaughton 2001; Vancook 2005; Goold 2008; Godwin 2010; Conly and Lee, 2010 unpublished data). Hogarth is non-stratified, oxygenated and highly enriched in dissolved sulphate (1200-2000 mg/L), resulting in chronic sulphate toxicity. On the other hand, Caland, which until recently hosted a commercial fish farm, is non-toxic and has an upper oxygenated fresh water lens that overlies an anoxic and moderately saline (200-500 mg/L sulphate) water column.

1.4 Objectives

The purpose of the project was to assess whether a permeable reactive barrier (PRB) could be used to reduce sulphate and metal concentrations in pit lake waters from the former Steep Rock iron mine site in Atikokan, Ontario. This was accomplished using batch reactor and flow-through reactor experiments in order to assess the ability of various different organic substrates to induce bacterial sulphate reduction in order to lower sulphate concentrations in waters from the pit lakes. The flow-through reactor experiments were designed to simulate a permeable reactive barrier at the laboratory scale.

CHAPTER 2: EXPERIMENTAL AND ANALYTICAL METHODS

2.1 Batch Reactor Experiment Design

Batch reactor experiments were conducted using 500 mL, wide mouth, opaque HDPE Nalgene bottles (Fig. 2.1), which were sterilized with ethanol prior to conducting experiments. The bottles were filled with the following treatments:

Treatment 1: 15% organic matter (either cow manure, horse manure, peat, composted straw or wood chips), 15% creek sediment (the SRB source), 40% till (non-reactive medium) and 30% carbonate rock (Mosher Carbonate).

Treatment 2: 20% organic matter, 45% till and 35 % carbonate rock.

Treatment 3: 15% organic matter, 15% molasses (as a nutrient for SRB), 40% till and 30% carbonate rock.

Control: Hogarth 18 m water only.

An attempt was made to homogenize the initial organic and inorganic materials, by using a smaller grain size with a range of 0.00 phi to -1.00 phi (1.0-2.0 mm) for glacial till and for carbonate rock. The smaller grain size allowed for greater homogeneity when mixing the reactive media in each of the treatments.

The experiment was conducted for six months and samples were kept at room temperature (~ 20^{o}C). Samples were analyzed at 1, 2, 3, and 6 months for H_2S, pH, Eh (redox), alkalinity, conductivity, metals and sulphate. Each bottle was mixed at a 1:1 mass ratio (250 g reactive mixture to 250g water) by weight on a Mettler Toledo scale (0.01g). Once the bottles were sealed, they were not reopened until the sampling date. The water used for the experiment was taken at an 18 m depth from Hogarth Lake.

The following bottles were used in the batch were used in the batch reactor experiments:

- Treatment 1:
  - Cow manure (duplicates at weeks 4, 12 and 24); horse manure (duplicates at weeks 4 and 8), peat (duplicate at week 12), composted straw (duplicates at 8 and 24 weeks) and wood chips (duplicate at 12 weeks).

- Treatment 2:
  - Cow manure (duplicates at weeks 4, 12 and 24); horse manure (duplicates at weeks 4 and 8), peat (duplicate at week 12), composted straw (duplicates at 8 and 24 weeks) and wood chips (duplicate at 12 weeks).

- Treatment 3
  - Cow manure (duplicates at weeks 4, 12 and 24); horse manure (duplicates at weeks 4 and 8), peat (duplicate at week 12), composted straw (duplicates at 8 and 24 weeks) and wood chips (duplicate at 12 weeks).

- Water only (duplicates at weeks 5, 8 and 24 weeks).

Bottles were placed on a "shaker" table to ensure constant mixing of the water and reactive media (Fig. 2.1). Samples were inverted once a week to prevent settling of the reactive media.

Figure 2.1: Photograph of batch reactors on shaker table.

2.2 Flow-Through Reactor Design

Flow-through experiments were designed to simulate a PRB at the laboratory scale (Fig. 2.2). The reactive media chosen for the flow-through experiments were based on the results of the batch experiment. The flow-through reactors were filled with different combinations of the creek sediment (SRB source), till, carbonate rock, and a mixture of horse manure and wood chips. The materials were taken from the same sources used in the batch experiments (see section 2.1a). Homogenized silica sand was used as a non-reactive medium to separate layers within the reactors and also used at the inflow and outflow of the reactor to prevent clogging of the materials (e.g., Waybrant et al., 2002; Gilbert et al., 2004). Also, 300 μm and 25 μm nylon screen were added at the inflow and outflow ports of each of the reactors to prevent clogging of the tubing. All tubing consisted of laboratory grade tygon tubing.

Glacial till, with a grain size range of -2.00 phi to 3.00 phi (4.0-8.0 mm) was used to increase the porosity and provide permeability of the reactive media and allow water flow freely through the reactors (e.g., Lyew and Sheppard, 1999; Tsukamoto et al., 2004). Coarse carbonate sand was produced by crushing and sieving Mosher Formation carbonate rock to a grain size between -1.50 phi and -3.00 (2.8-3.0 mm). The carbonate sand apart from being the primary source of alkalinity, also provided increased porosity and permeability.

Figure 2.2: Flow-through column design. (1) Source water; (2) peristaltic pump; (3) flow-through reactor columns; (4) 10-port manifold; (5) flow-through cells; (6) syringe used for extracting sample; (7) cleansing water; (8) waste containers.

The relative portion of the material used in the reactive mixtures (7.5% horse manure, 7.5 % wood chips, 15% creek sediment, 40% till and 30% carbonate rock) for each reactor was based on the mass calculated from the results of the batch reactor experiment results. Carbonate sand and silica sand were added to the flow-through reactors to create different reactive “chambers” (Fig. 2.3). The chambers were used to represent separate reactive trenches within a full-scale PRB (e.g., Neculita et al., 2007).

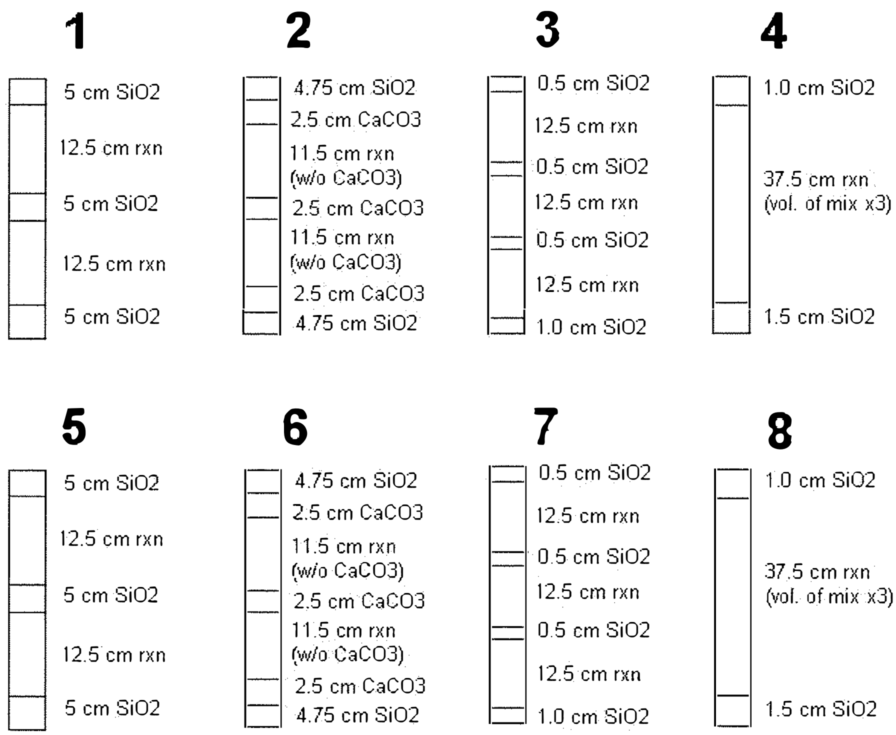


Figure 2.3: Schematic diagram showing the internal structure of the flow-through reactors. Reactors 5 through 8 are duplicates of reactors 1 through 4, respectively. Reactors 1 and 5 had two reaction chambers separated by silica sand; reactors 2 and 6 had two chambers separated by carbonate rock; reactors 3 and 7 had three chambers separated by silica sand; and reactors 4 and 8 had a single chamber.

Flow-through reactors 1 and 5, 2 and 6, 3 and 7, and 4 and 8 had the same combinations of the reactive media to allow for comparison. Reactors 1 and 5 had two reaction chambers separated by silica sand. Reactors 2 and 6 had two reaction chambers separated by carbonate sand, and carbonate sand was also added at the influent and effluent, although carbonate sand was not added to the reactive medium. Reactors 3 and 7 had three reaction chambers separated by silica sand. Reactors 4 and 8 had a single reaction chamber.

A peristaltic pump was used to pump stock water through the bottom of the reactor (to minimize gravitational effects) at an average flow of 0.1 mL/min. The stock water was taken from the same location as the water used in the batch experiments; however, the water for the flow-through reactor experiments was taken from Hogarth pit lake at a later date and therefore there are slightly different parameter concentrations. The water was taken from a depth of 18 m; at this depth sulphate values increase in Hogarth pit lake and remain relatively constant to bottom (Goold, 2008).

Argon gas was pumped through the sample lines during sampling to maintain anaerobic conditions between samples. Distilled de-ionized water (DDW) was used to flush the system during sampling periods. At the outflow of each reactor, each tube was connected to a 10-port manifold (a port for the 8 reactors, one for argon gas and one for DDW) that connected each of the lines into a single line that drained into waste water collection jugs. Valves were in place at the inflow and outflow of each reactor, and at the junction where water flowed out of the manifold. This allowed the main line to be split into three different lines during sampling. The first line was connected to three flow-through electrode cells for in-line measurement of pH, redox, and conductivity/TDS. The second line was connected to a syringe in order for water to be extracted for analysis without allowing oxygen into the system. The third line was connected to the waste jugs. The weekly sampling procedure involved:

(i) Argon gas was turned on and allowed to run through the system.

(ii) DDW was run through the electrode and syringe lines to remove any residual material.

(iii) Inflow valves were shut-off to all reactors that were not being sampled.

(iv) Water from the reactor being sampled was allowed to run through the flow-through cell array for in-line measurements.

(v) Water from the reactor was run to the syringe line and the sample was taken for laboratory analysis.

(vi) Each line was flushed with DDW and the process was followed for the next flow-through reactor.

Reactors were wrapped in aluminum foil to prevent light infiltration, which might promote the growth of photolithotrophic bacteria. All joints and fixtures were sealed with parafilm wrap to ensure that the reactors were kept anaerobic. No effort was made to reduce the oxygen content of the influent water and; therefore, the dissolved oxygen content was in equilibrium with the atmosphere. This is the condition that is likely to be encountered in a full-scale barrier installed at the mine site.

Blowes et al. (2003) noted that organic carbon is commonly the least permeable component in a reactive mixture and in some cases it is necessary to increase the hydraulic conductivity of the mixture by including a coarse-grained material. Efforts were made in the design of the reactors to prevent clogging, such as using a larger grain size for both the till and the carbonate rock, as well as using silica sand and nitex/nylon screening at the influent and effluent ports.

2.3 Analytical Methods

Run-product waters from batch reactor and flow-through reactor experiments were analyzed using the same analytical methods unless otherwise stated. Analytical errors were calculated by the average errors based on repeated measurements of water-only batch experiments and initial stock water for the flow-through experiments. The standard deviations for all parameters can be found in Appendix 2.

2.3.1a Physical Water Quality Parameters

Redox Potential (Eh) and pH

For the batch experiments, the Nalgene bottles were placed in an anaerobic glove box that was flushed with nitrogen (N_2) gas prior to opening the bottles. The water from the bottles was filtered using a 100 μm nitex screen in order to remove most of the reactive media, and was transferred to silicone capped centrifuge tubes. Measurement of Eh was conducted using a Mettler Toledo LE501 electrode. A DG111-SC pH probe was used to record the pH of the samples in the batch experiments and a VWR symphony 3-in-1 pH electrode was used in the flow-through experiments.

Conductivity and Total Dissolved Solids

In the batch experiments, conductivity was measured using an Accumet XL60 Multimeter System. For the flow-through experiments, conductivity and TDS were measured with a VWR symphony two cell platinum conductivity probe. Total dissolved solids (TDS) were not measured in the batch experiments.

2.3.1b Major Anions

Alkalinity and Bicarbonate

Alkalinity (as $CaCO_3$) was determined by titration in the Lakehead University Environmental Lab. Samples were titrated with 0.01N H_2SO_4 to pH 4.5 with a DL53 Mettler Titrator and DL20. Data was recorded and analyzed using Lab X software. Bicarbonate as alkalinity was calculated from total alkalinity (TA) accordingly:

$$\text{Bicarbonate Alkalinity } (CaCO_3 \text{ mg/L}) = 50000(2TA-10^{-14+pH})/(1+2K_2 10^{pH})$$

where K_2 equals the second dissociation constant for carbonic acid, $10^{-10.3}$ (Steele, 2004). Samples were measured within 24 hours and were kept at room temperature.

Sulphate, Nitrate and Chloride

Samples were filtered using a 0.45 μm syringe filter, with 0.5 mL of the filtered sample being transferred to vials and diluted 10 times with DDW. Sulphate, nitrate and chloride concentrations were analyzed using a Dionex DX-120 Ion Chromatograph (IC) with an IonPac As14 Analytical Column AS40 Automater Sampler.

Sulphide

For the determination of sulphide (H_2S), centrifuge tubes containing the treatment were centrifuged for approximately 30 minutes to remove particulate matter and 15 mL of sample was filtered through a 0.45 μm syringe filter into amber glass vials with silicone caps. Each sample was preserved with zinc acetate and sodium carbonate and 10 mL of the sample was poured into a 100 mL flask, along with 2 mL of 0.025N iodine solution and 0.2 mL of 50% HCl. Starch solution was added to the mixture and the solution was titrated with 0.01N sodium thiosulphate in order to calculate the concentration of the initial sulphide stock. 15 mL of the samples were poured into test tubes and mixed in a vortex mixer with 1.0 mL of amine-H_2SO_4 reagent and three drops of ferric chloride. After 3-5 minutes, 3.0 mL of diammonium hydrogen phosphate solution was added. The final solution was analyzed for H_2S using a Varian Cary 5E Spectrophotometer. A linear regression using the standard concentrations versus the absorbance was performed using QPRO. The concentration of each sample was then calculated using the data from the regression (see Appendix 1 for reagents and standards). For the flow-through experiments, hydrogen sulphide was measured by the same method as the batch experiments for weeks 1 and 2. No sulphide data were acquired for weeks 3, 4 and 5 due to difficulties with the instrument; and sulphide was measured by titration with 0.005 N thiosulphate for the remainder of the experiment.

2.3.1c Major Cations and Metals

A sample aliquot of 10 mL was added to centrifuge tubes and preserved with 0.4 mL HNO_3. The water sample was digested and brought to 10 mL with distilled deionized water (DDW). The 10 mL diluted sample was then analyzed on a Varian Vista Pro Inductively Coupled Argon Plasma Spectrometer (ICP) with Cetac Autosampler. Major cations include calcium, magnesium, sodium and potassium, while the metals analyzed were aluminum, arsenic, barium, cadmium, copper, cobalt, chromium, iron, nickel, manganese, lead, sulphur and vanadium.

2.3.2 Organic Material Analysis

Organic materials were analyzed for trace metal contents by ICP-AES and C-N-S contents by LECO at the Lakehead University Forest Soils Laboratory. Prior to either analysis, samples were dried at 70^{o}C in an oven until a constant mass was achieved, and then ground through a Wiley mill to 40 mesh size. Dry matter percent was determined gravimetrically by drying the ground samples for another 2 hours at 105^{o}C.

The acid digestion method is a modification of Miller (1998), where a 0.2 g soil sample is digested in 6 mL of HNO_3 and 2 mL of HCl for 8 hours at 90°C in a block digester. Distilled deionized water is added to the acid to dilute the digest to 100 mL. The test tubes are shaken end over end to mix the solution well and then the solution is filtered to remove any remaining particles. The elemental concentration of the clear filtrate was determined using an inductively coupled plasma atomic emission spectrometry (ICP-AES).

Combustion analysis of C, N and S is modified from Horneck and Miller (1998). Approximately 0.2 g of sample is weighed and run using a LECO CNS-2000 Analyzer (a non-dispersive, infrared microcomputer-based instrument). The instrument converts any elemental carbon, nitrogen and sulphur into CO_2, N_2, NO_x and SO_2. The combustion gases are swept out of the combustion chamber and allowed to equilibrate before being released through an infrared detection cells (IDC) and aliquot doser. The voltage from the IDC is read and processed by the computer and produces the analysis for carbon and sulphur. The sample gas in the Aliquot Doser is transferred by a He carrier gas to a catalyst heater where NO_X gases are reduced to N_2. Lecosorb is used to remove CO_2 and anhydrone to remove H_2O that leaves only N_2 gas and He.

The gases are compared and results in an output voltage, which is read and processed by the computer and produces the measurement for nitrogen.

2.3.3 Analysis of Non-Organic Constituents

2.3.3a X-ray Diffraction Analysis

Powder X-ray diffraction (XRD) analysis was performed using a Pananalytical Expert Pro Diffractometer to determine the mineralogy of the initial materials, as well as the final flow-through reactor material. Each sample was first ground to powder using a mortar and pestle to a sample size of <75 μm. Alpha aluminum oxide (α-Al_2O_3) was added (10% by mass; +/- 0.0001 g) to the milled sample in order to correct for peak offsets and quantification of phases. The powder was then loaded into cavity mounts and a spinner stage was used to limit preferred orientation. Diffraction patterns were obtained using CuKα radiation, with generator settings of 40 mA and 45 kV, and scanning from a 2θ of 4° to 90° with a step size for the scan was 0.0070 ^{o}2-theta and a scan step time of 67.3 s/ ^{o}2-theta. Samples were processed using Panalytical's High Score Plus Software and ICDD database PDF-2.

2.3.3b Acid Digestion Analysis

Acid digestion was completed for the organic materials, as well as the initial carbonate rock, till and creek sediment (SRB source) using a modification of US Environmental Protection Agency (EPA) method 3050B (United States EPA, 1996). Samples were dried at approximately 40 ^{o}C and ground using an alumina mortar and pestle. Approximately 0.5 grams of sample were digested with approximately 8 mL of HNO_3 and refluxed for 2 hours and then reduced to 5 mL. Once samples had cooled, approximately 5 mL of H_2O_2 was added in 1 mL aliquots and refluxed for 2 hours. Samples were cooled, brought up to 5 mL with HCl and refluxed for 2 hours. All refluxing was conducted in closed, 30 mL Teflon reactor vials. Samples were cooled and filtered through Whatman No. 42 filter paper into a 100 mL volumetric flask. Once filtered, the samples were made to volume with deionized water and analyzed by ICP-AES at the Lakehead University Instrumentation Laboratory.

CHAPTER 3: RESULTS

3.1 Characterization of Initial Materials

3.1.1 Hogarth Pit Lake Water

The chemistry of the water used in the batch reactor and flow-through reactor experiments are listed below and the water used for the batch and flow-through experiments is comparable to the average composition of Hogarth pit lake for all seasons between 2005 and 2008 (Table 3.1).

Table 3.1: Chemistry of Hogarth pit lake 18 m water used for batch and flow-through reactor experiments; and 2005-2008 (average all seasons) water chemistry for Hogarth pit lake 18 m (data from Goold, 2008, Godwin, 2010; Conly and Lee, unpublished data).

Description	Batch Expt. (Summer 2008)	Flow-Through Expt. (Winter 2009)	Hogarth (2005 – 2008 avg.)
pH	6.9	7.9	7.0
Conductivity (uS/cm)	2329	2301	2313
Redox (mV)	114.9 mV	278.7	-
Sulphide (mg/L)	<0.10	0.05	-
Alkalinity (mg/L)	121.7	150.1	122.9
SO_4^{2-} (mg/L)	1423	1592	1585
Cl^- (mg/L)	12.9	16.0	13.2
Ca (mg/L)	316.3	320.0	308.0
Mg (mg/L)	178	173	177.2
Na (mg/L)	23.5	23.6	21.70
K (mg/L)	6.46	6.80	6.10
Al (mg/L)	<0.005	0.013	0.015
Ba (mg/L)	0.007	0.008	0.006
Cu (mg/L)	<0.002	0.001	0.007
Fe (mg/L)	0.046	0.005	0.038
Mn (mg/L)	0.168	0.061	0.054
Ni (mg/L)	0.034	0.035	0.033
Pb (mg/L)	<0.005	0.013	0.090
S (mg/L)	506	507	461

The minimum detectable limits and standard deviations for all parameters are provided in Appendix 2.

3.1.2 Composition of Non-Organic materials

3.1.2a Mineralogy

X-ray diffraction patterns for creek sediment, glacial till and carbonate rock are shown in Figures 3.1, 3.2 and 3.3. Run conditions and the nature of the materials allows for the XRD to identify minerals that have modal abundances >2%, thus some accessory and trace minerals are not identified. Creek sediment is composed of quartz, and potassium feldspar. Glacial till is composed of quartz, plagioclase feldspar, chlorite, potassium feldspar, amphibole (undifferentiated) and phlogopite. The Mosher Carbonate rock is composed primarily of calcite and dolomite with minor amounts of quartz.

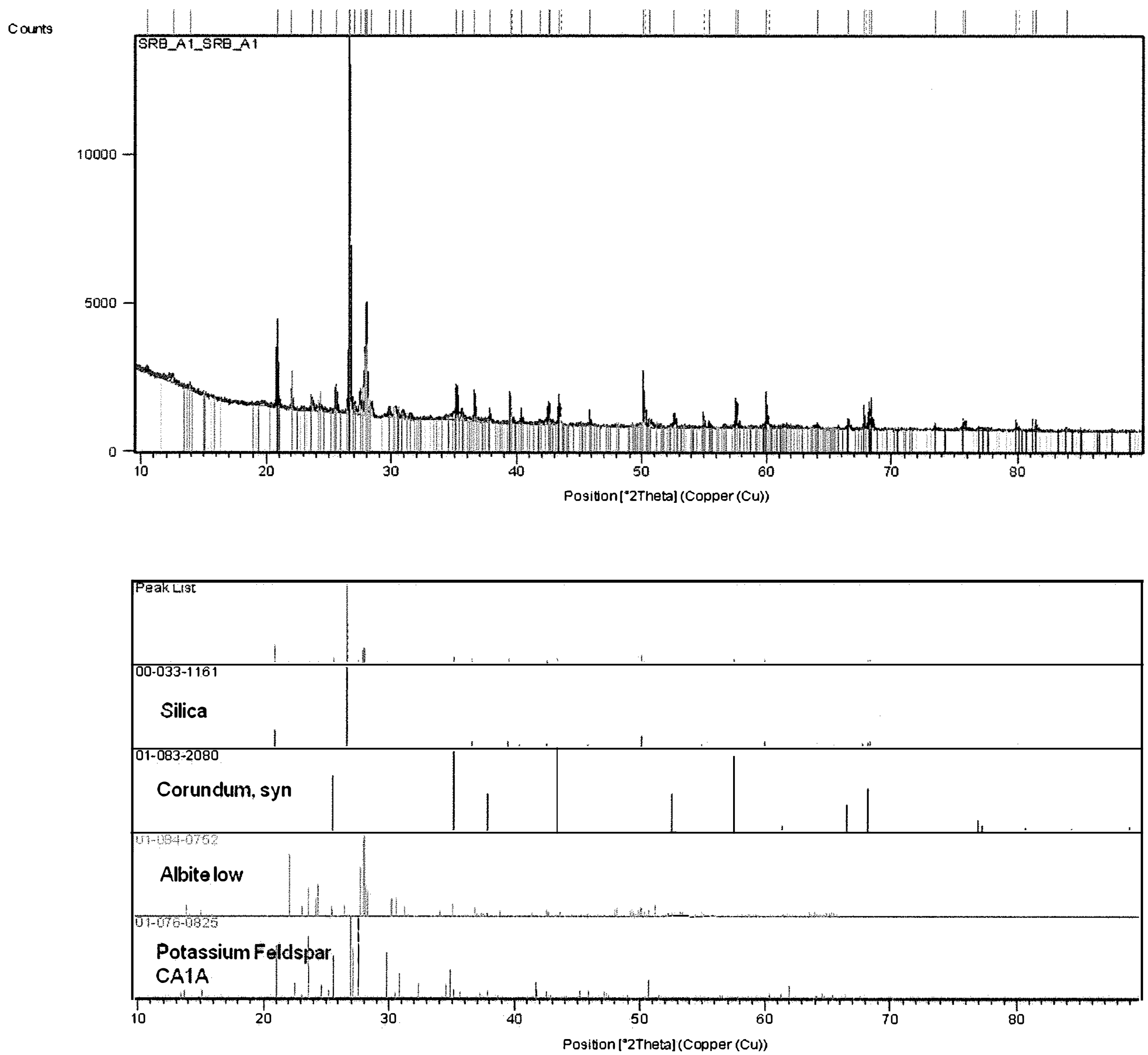


Figure 3.1: X-ray diffraction pattern of creek sediment (SRB source) used in the batch and flow-through reactor experiments.

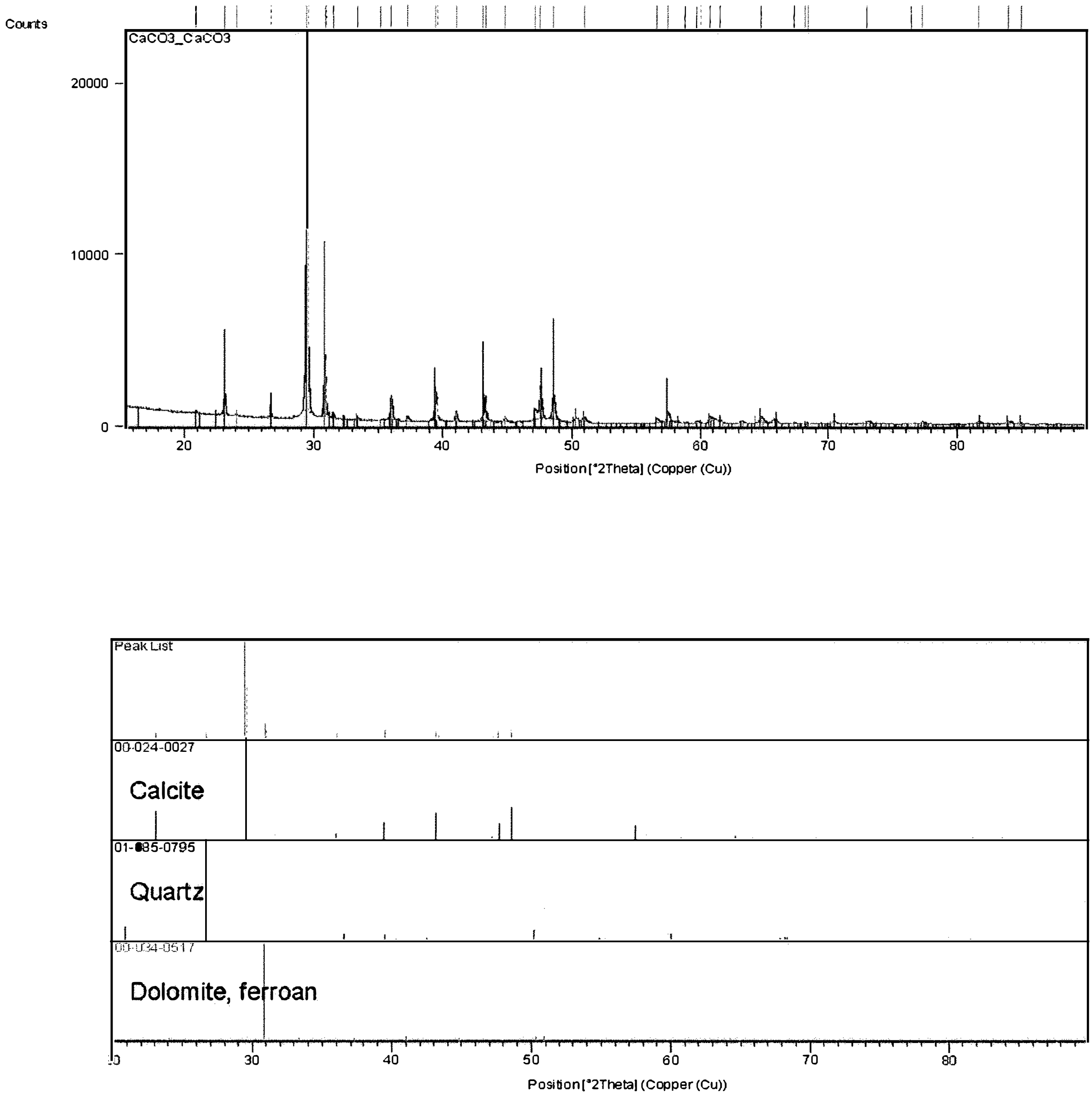
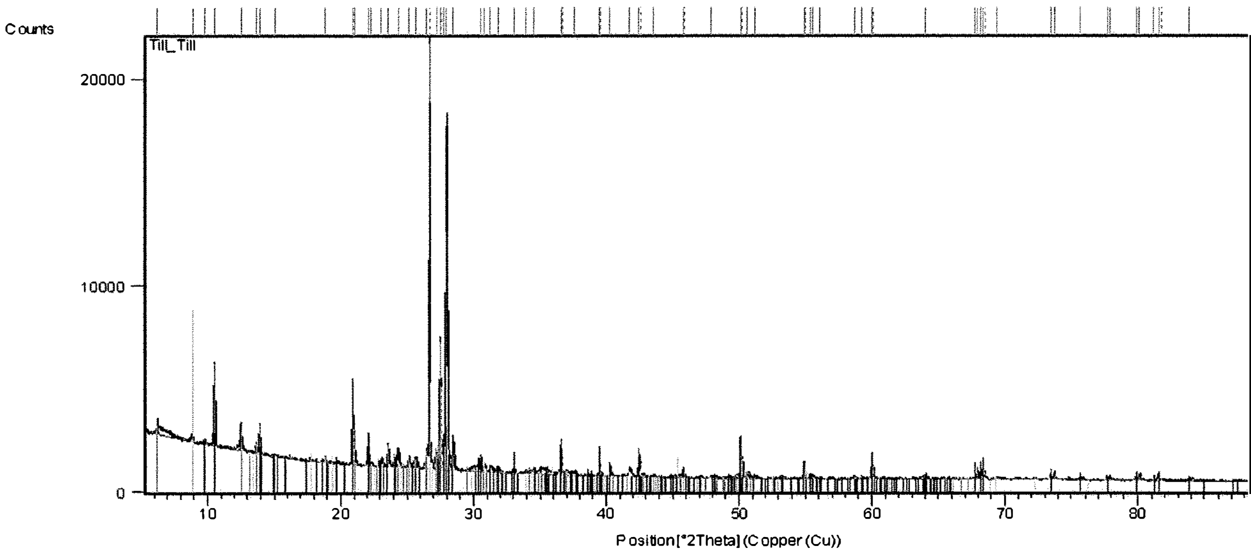


Figure 3.2: X-ray diffraction pattern of Mosher carbonate rock used in the batch and flow-through reactor experiments.



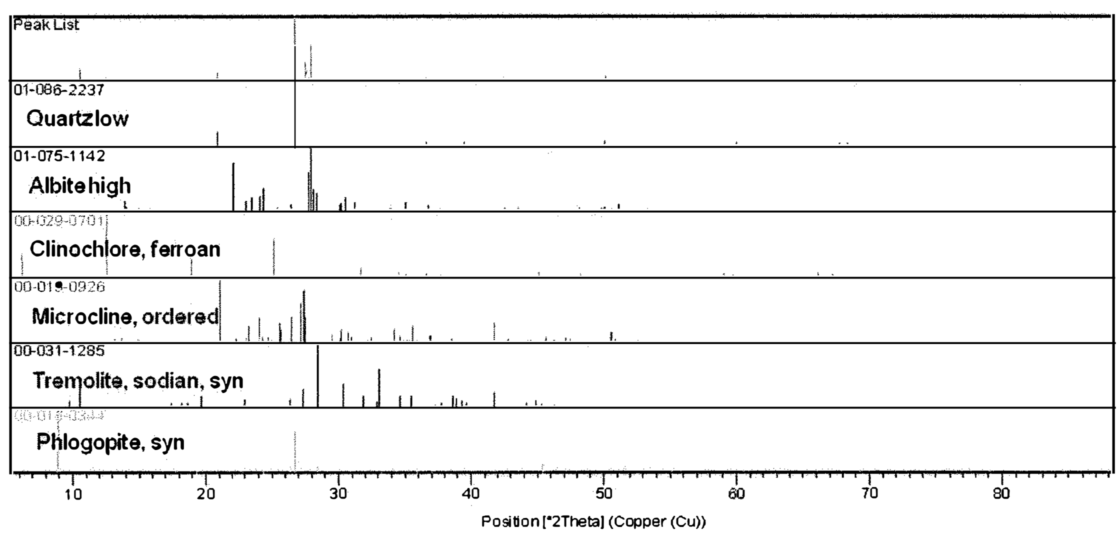


Figure 3.3: X-ray diffraction pattern of glacial till used in the batch and flow-through reactor experiments.

3.1.2b Acid Soluble Composition

The composition of the non-organic materials used in the batch and column reactor experiments is listed below (Table 3.4).

Table 3.4: Acid soluble composition of non-organic materials (ppm).

Description	Mosher Carbonate Rock	Creek Sediment	Glacial Till
Aluminum	63.9	18700	10500
Arsenic	<0.05	5.90	<0.05
Boron	0.18	16.5	6.25
Barium	2.79	125.3	60.2
Beryllium	<0.01	0.16	<0.01
Cadmium	<0.02	<0.02	<0.02
Calcium	250800	12300	6930
Chromium	<0.02	4.53	37.9
Cobalt	<0.02	12.6	7.98
Copper	<0.01	29.6	25.7
Iron	7290	70400	44500
Lead	<0.03	17.9	4.83
Magnesium	18300	10700	10900
Manganese	3710	655	1090
Molybdenum	<0.02	<0.02	<0.02
Nickel	<0.01	38.17	49.6
Phosphorus	<0.04	470.8	602.3
Potassium	38.6	2960	1620
Sulphur	350	327.5	36.2
Selenium	<0.05	<0.05	<0.05
Sodium	93.4	1820	743
Strontium	60.2	32.2	34.6
Thallium	<0.05	<0.05	<0.05
Tin	<0.05	<0.05	1.15
Titanium	1.55	1650	1110
Vanadium	<0.03	85.3	41.6
Zinc	<0.05	90.3	33.7

All concentrations are in parts per million (ppm), unless otherwise stated.

The total acid soluble composition of the initial reactive media (carbonate, glacial till and creek sediment) are given in Table 3.5.

Table 3.5: Acid Soluble composition for metals of initial reactive media (ppm).

Description	Concentration
Aluminum	7180
Boron	6.00
Calcium	8270
Copper	19.0
Iron	3.09
Magnesium	10700
Manganese	1680
Phosphorus	582
Potassium	1920
Sulphur	328
Sodium	673
Zinc	36.0

The acid soluble composition of the final flow-through reactor media (post-experiment) are given in Table 3.6.

Table 3.6: Acid Soluble composition for select metals of flow-through reactor media (ppm).

Metal	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Reactor 5	Reactor 6	Reactor 7	Reactor 8
Aluminum	2840	1740	1310	6810	1850	1560	2660	2650
Boron	3.30	2.50	3.70	7.30	2.50	2.40	50	3.90
Calcium	72500	36800	73600	73100	45800	55200	53500	118000
Copper	3.50	0.60	1.60	9.60	0.70	6.40	2.30	5.20
Iron	11400	5740	7610	19400	4860	4960	8050	12700
Potassium	746	523	345	1339	632	479	768	678
Magnesium	9290	4560	7520	13700	4950	6120	5900	12100
Manganese	1280	620	1250	1430	721	938	867	1890
Sodium	269	147	143	359	224	98	243	298
Phosphorus	112	59.0	59.0	356	62.0	46.0	86.0	128
Sulphur	3110	1680	1480	2700	1150	1110	2120	2530
Zinc	11.6	5.30	4.60	26.0	2.90	7.80	9.90	15.3

3.1.3 Composition of Organic Materials

The trace element and carbon-nitrogen-sulphur composition of the organic materials used in the batch and flow-through experiments are provided in Tables 3.7 and 3.8, respectively.

Table 3.7: Composition of organic matter used in batch and flow-through experiments (ppm)

Metal	Peat	Cow Manure	Horse Manure	Composted Straw	Wood Chips
Aluminum	2120	1760	1970	4740	16.5
Boron	4.4	27.3	15.8	33.0	0.30
Calcium	12200	24500	7400	36500	1700
Copper	17.2	50.6	52.4	143	2.6
Iron	5639	3653	4079	20952	58.7
Potassium	100	36700	10200	14900	700
Magnesium	1100	7500	2800	8400	300
Manganese	109	202	290	432	35.7
Sodium	200	5500	500	2100	500
Phosphorus	400	7300	3500	8700	100
Sulphur	1720	4840	2020	4260	94.2
Zinc	11.4	171	106	294	12.7

Table 3.8: Carbon, nitrogen and sulphur contents of organic matter used in batch and flow-through experiments

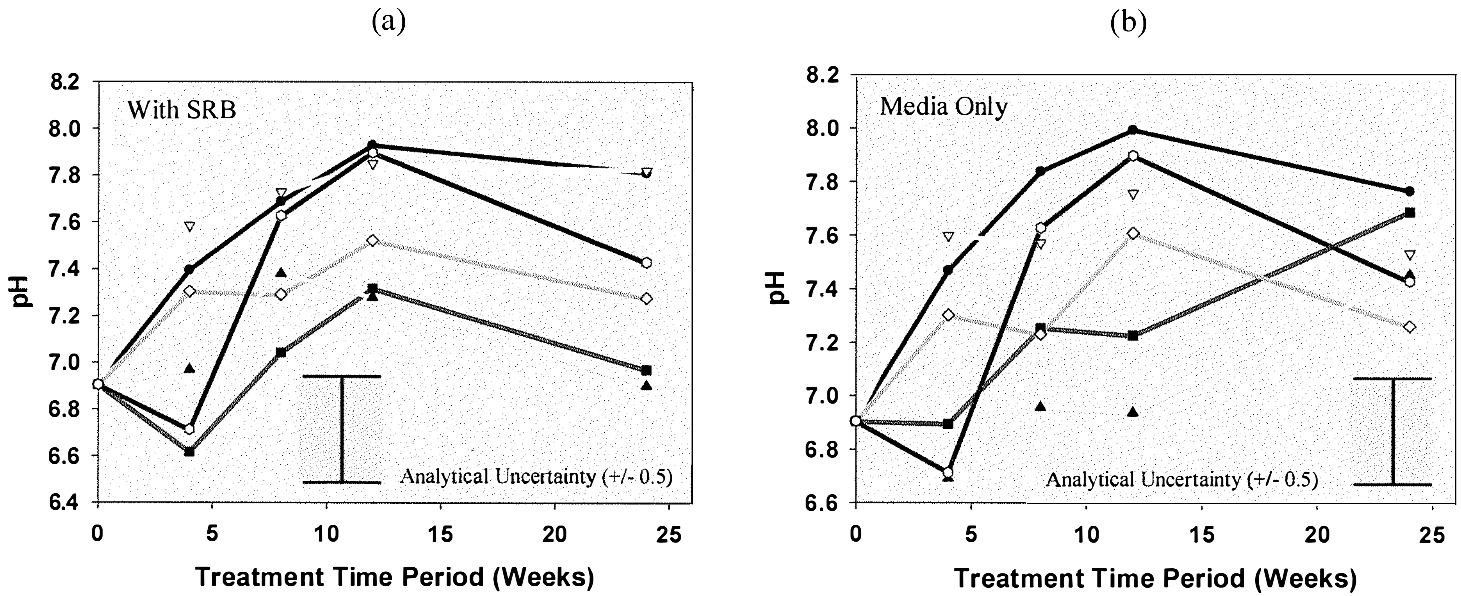
Parameter	Peat	Cow Manure	Horse Manure	Composted Straw	Wood Chips
Weight (g)	0.208	0.200	0.199	0.198	0.206
Carbon%	51.9	39.1	43.5	27.8	50.4
Sulphur %	0.18	0.53	0.23	0.42	0.01
Nitrogen%	2.20	4.00	2.00	3.60	0.11

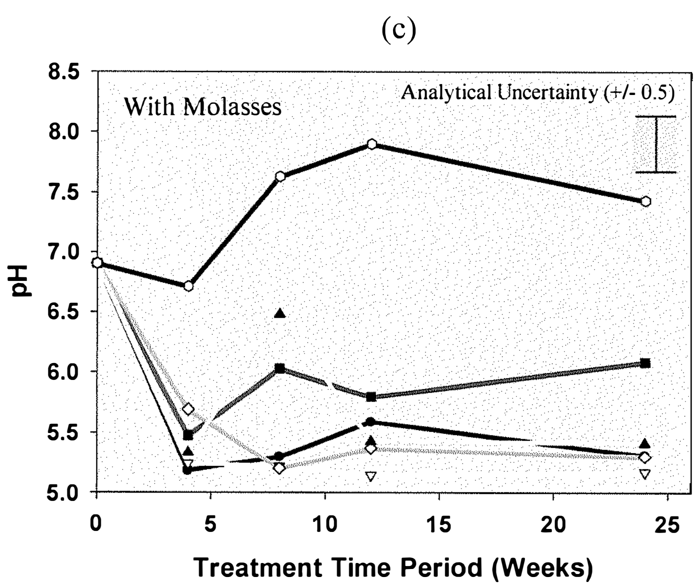
3.2 Results for Batch Reactor Experiments

Time series graphs (Figs. 3.14-3.16) for batch reactor experiments are shown below and the raw data is provided in Appendix 3.

3.2.1 Physical Water Quality Parameters

pH: The pH for all organic media in both treatment 1 (Fig. 3.4a) and treatment 2 (Fig. 3.4b) showed a general increase, while for treatment 3 pH values decreased (Fig. 3.4c). Increases in pH for water-only were observed in all three treatments. The largest increase was observed for composted straw and cow manure in treatments 1 and 2, while in treatment 3, composted straw had the lowest decrease. Cow manure pH values in both treatment 1 and 2 increased from 6.9 to 8.0 at week 12 and decreased to 7.8 for the remainder of the experiment. An increase in pH for composted straw from 6.9 to 7.8 at 24 weeks was observed in treatment 1, whereas an initial increase from 6.9 to 7.7 at week 12 was observed in treatment 2 and remained relatively constant for the remainder of the experiment. pH for horse manure initially increased from 6.9 to 7.5 (treatment 1) and 6.9 to 7.6 (treatment 2), but decreased slightly (pH = 7.3) at week 24 in both treatments. Peat pH values in treatment 2 increased throughout the experiment from 6.9 to 7.7, whereas the values in treatment 1 increased from 6.9 to 7.3 for the first 12 weeks and decreased to 7.0 by week 24. Wood chip pH values in treatment 1 increased from 6.9 to 7.4 in the first 8 weeks before decreasing to 6.9 at week 24. Wood chip pH values in treatment 2 indicated a





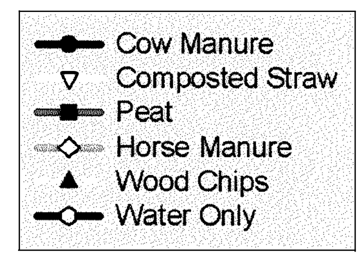
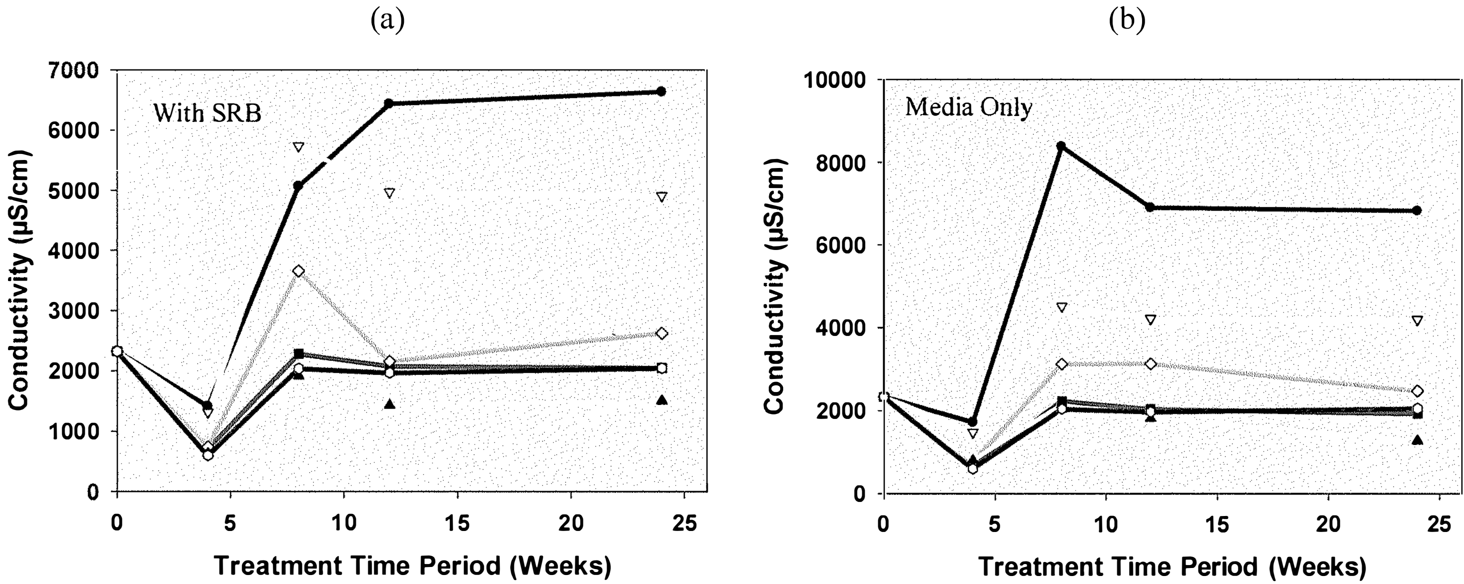


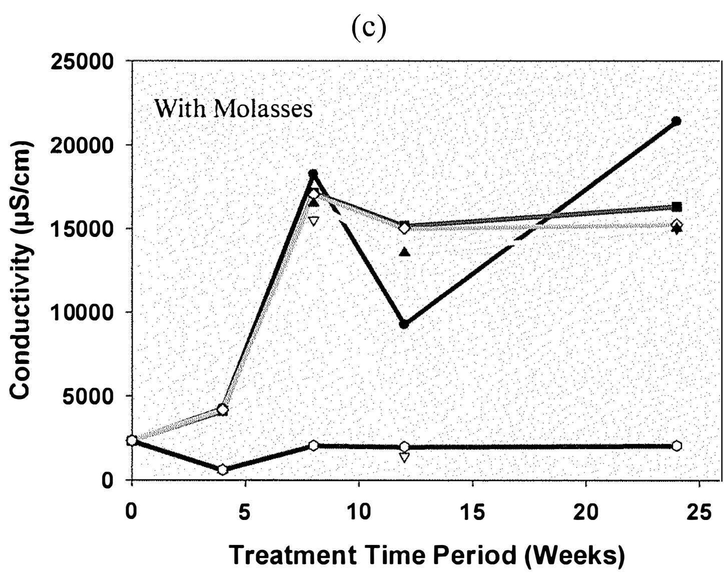
Figure 3.4: Variation in the pH of batch reactor waters over the duration of the experiment. (a) pH treatment which includes the addition of a SRB source to the reactive media. (b) pH for treatment 2 (reactive media only). (c) pH for Treatment 3, which includes the addition of molasses to the reactive media.

progressive increase from 6.9 to 7.5. Treatment 3 pH values for cow manure, wood chips, horse manure and composted straw all showed a decreasing trend from 6.9 to between 5.0 and 5.5 throughout the experiment. Treatment 3 pH values for peat decreased to 5.5 between weeks 1 and 4, but increased for the remainder of the experiment to 6.0.

Conductivity: Conductivity values for water-only, peat and wood chips in both treatment 1 (Fig. 3.5a) and treatment 2 (Fig. 3.5b) decreased between weeks 1 and 4, but then returned to approximately initial values (2300 μS/cm) for the remainder of the experiment. All conductivity values in treatment 3, other than water-only, (Fig. 3.5c) experienced a significant increase to >15000 μS/cm by the end of the experiment. Values for composted straw in treatments 1 and 2 initially decreased to approximately 1400 μS/cm, before increasing to 5000 (treatment 1) and 4000 (treatment 2) μS/cm at week 24, respectively. Conductivity values for cow manure in treatments 1 and 2 exhibited the greatest increases. Although, values for both treatments decreased between 1 and 4 weeks, conductively increased for the remainder of the experiment with final values of 6600 and 6800 μS/cm for treatments 1 and 2, respectively.

Reduction Oxidation Potential (Redox): Redox values in all treatments decreased, except water-only which showed a slight increase, throughout the experiment. Treatment 1 (Fig. 3.6a) redox values for composted straw and cow manure displayed a minor increase at week 4, but decreased to -270 mV (cow manure) and -280 mV (composted straw) at the end of 24 weeks. Redox values for treatment 1 with wood chips also showed a slight increase at week 4, decreased to approximately -200 mV at week 8, but increased to -144 mV at week 24. Values for horse manure and peat in treatment 1 decreased throughout the experiment to of -202 mV (horse manure) and -102 mV (peat) at week 24, respectively. Treatment 2 redox values (Fig. 3.6b) decreased throughout the experiment, with values of -199 mV (cow manure), -176 mV (horse





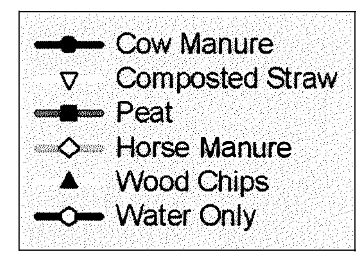
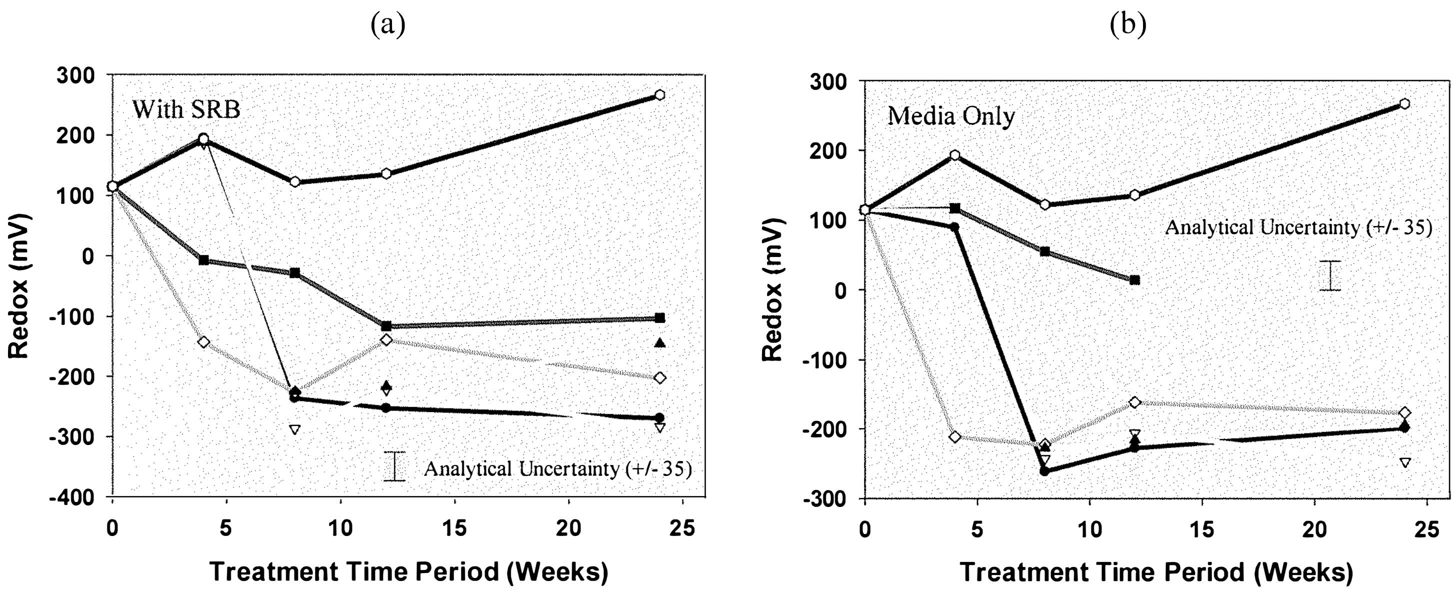
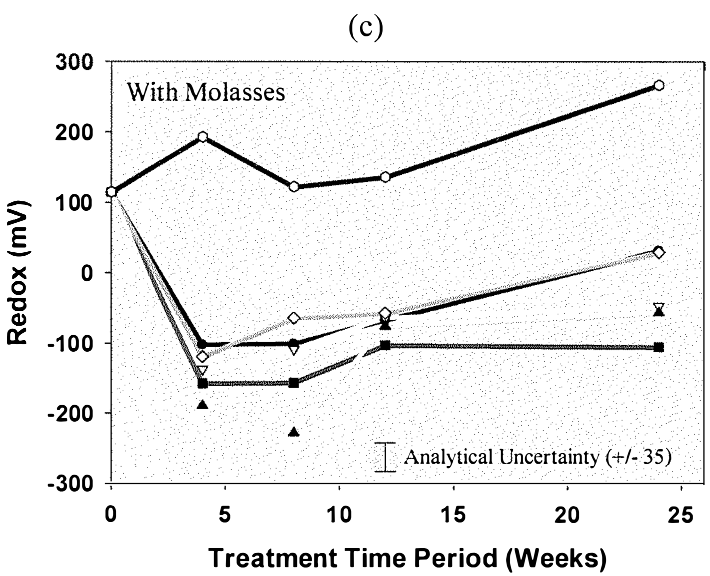


Figure 3.5: Variation in the conductivity of batch reactor waters over the duration of the experiment. (a) Treatment 1, which includes the addition of a SRB source to the reactive media. (b) Treatment 2 (reactive media only). (c) Treatment 3, which includes the addition of molasses to the reactive media. Analytical uncertainty (+/- 158) is less than symbol size.





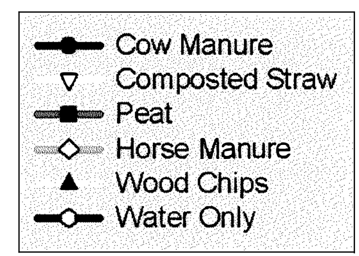


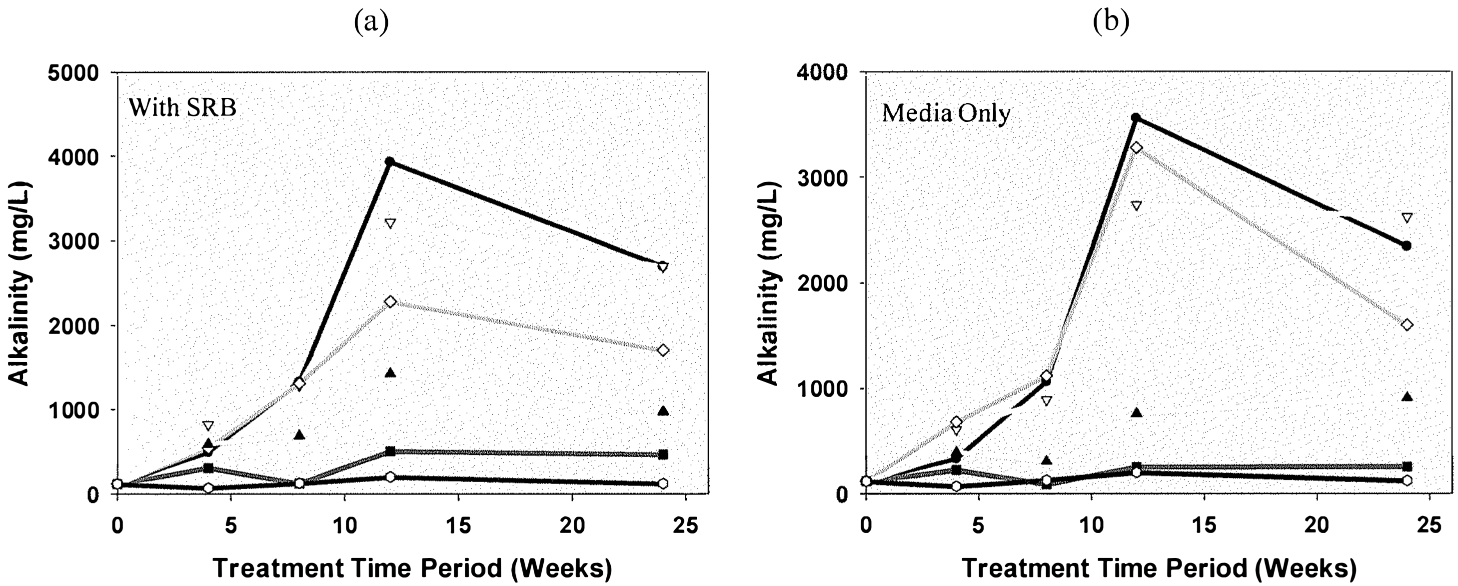
Figure 3.6: Variation in the redox of batch reactor waters over the duration of the experiment. (a) Treatment 1, which includes the addition of a SRB source to the reactive media. (b) Treatment 2 (reactive media only). (c) Treatment 3, which includes the addition of molasses to the reactive media.

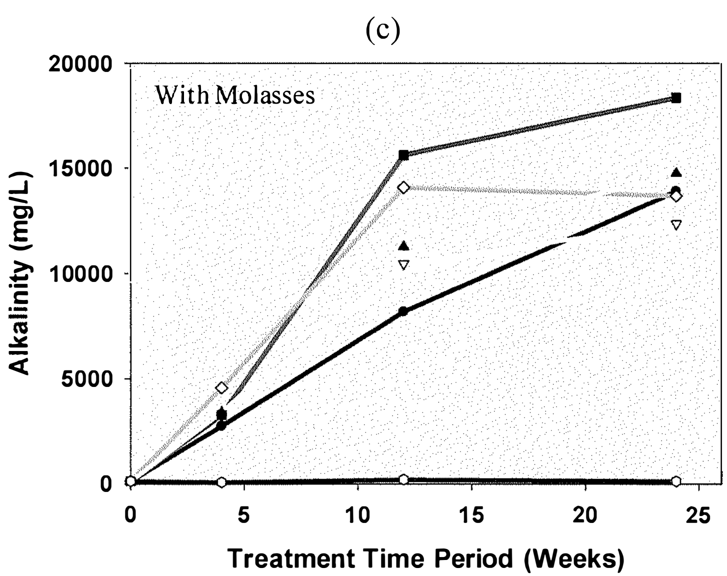
manure), -247 mV (composted straw) and -194 mV (wood chips) at the end of 24 weeks. There were no redox values for peat in treatment 2 at week 24, but values showed an initial decrease to 14.6 mV at week 12. Redox values for treatment 3 (Fig. 3.6c) all experienced an initial decrease to less than 100 mV at week 4, but values increased to 31 mV (cow manure), 32 mV (horse manure), -47 mV (composted straw), -56 mV (wood chips) and -105 mV (Peat) at week 24.

3.2.3 Major Anions

Total alkalinity (as $CaCO_3$): Total alkalinity shows similar trends for all treatments (Fig. 3.7). Alkalinity progressively increased in all treatments, although some of the reactive media for treatments 1 and 2 underwent a minor decrease in alkalinity at the end of the experiment. Cow manure and composted straw had the greatest increase on the whole in treatment 1 to approximately 2700 mg/L, whereas composted straw had the greatest increase in treatment 2 to approximately 2600 mg/L. No data was available for week 8 of treatment 3 due to a shortage in water from the reactor (Fig. 3.11c). All concentrations had a significant increase in alkalinity/bicarbonate, which progressively increased throughout the experiment. Peat had the greatest increase from 122 mg/L to 18300 mg/L and all other treatments increased from 122 mg/L to greater than 12000 mg/L. Concentrations for water-only remained relatively similar to initial values in all treatments.

Sulphate: Sulphate concentrations for treatment 1 (Fig. 3.8a) and treatment 2 (Fig. 3.8b) decreased for all reactive media, with the exception of peat, which remained relatively stable throughout the experiment, except for week 8. An increase was observed at week 8 for cow manure in treatment 2 and for peat in both treatments. In both treatments, composted straw and cow manure began to show signs of sulphate reduction after 12 weeks. Sulphate concentrations in both cow manure and composted straw were <5 mg/L at week 24 in treatment 1, whereas





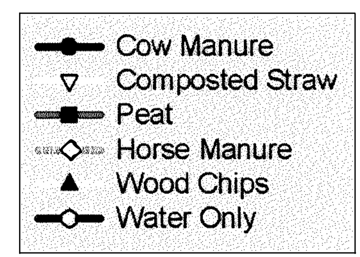
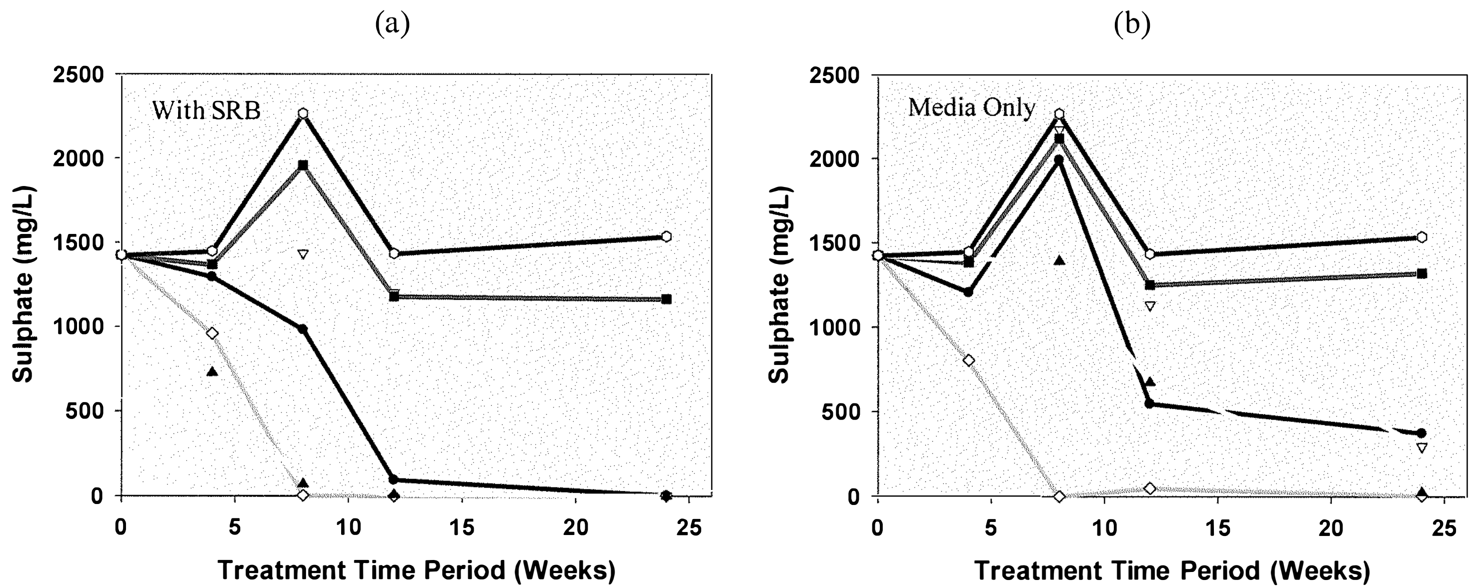
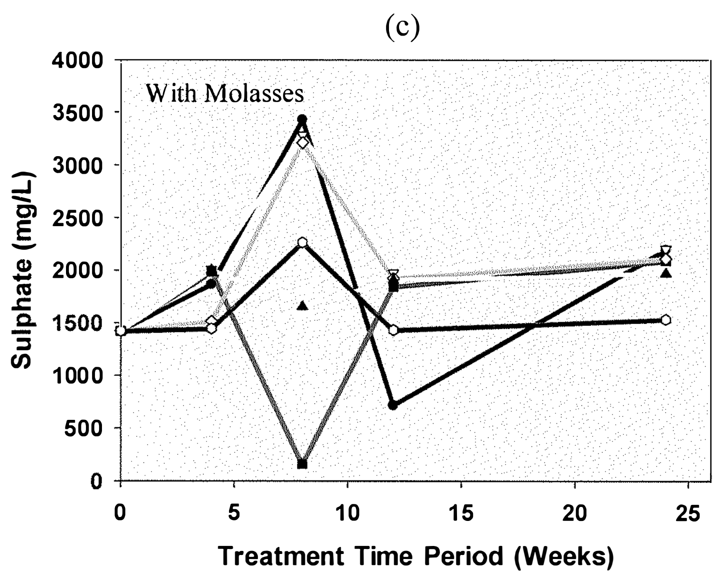


Figure 3.7: Variation in the alkalinity of batch reactor waters over the duration of the experiment. (a) Treatment 1, which includes the addition of a SRB source to the reactive media. (b) Treatment 2 (reactive media only). (c) Treatment 3, which includes the addition of molasses to the reactive media. Analytical uncertainty (+/- 27.2) is less than symbol size.





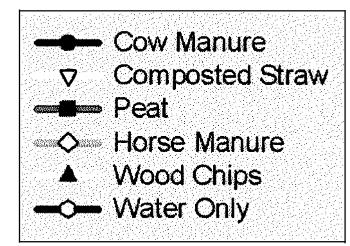


Figure 3.8: Variation in the sulphate content of batch reactor waters over the duration of the experiment. (a) Treatment 1, which includes the addition of a SRB source to the reactive media. (b) Treatment 2 (reactive media only). (c) Treatment 3, which includes the addition of molasses to the reactive media. Analytical uncertainty (+/- 51.3) is less than symbol size.

sulphate concentrations for wood chips and horse manure decreased to >99% by 8 weeks, whereas it took 24 weeks for concentrations in composted straw and cow manure to reach >99% sulphate reduction. For treatment 2, horse manure and wood chips were the most successful hosts for sulphate reducers with >99% decreases at 4 weeks and 24 weeks, respectively. Cow manure and composted straw each exhibited a decrease in sulphate concentrations to 300 mg/L (79% removed) and 375 mg/L (74 % removed), respectively. Peat, although there was a slight decrease, was not as successful at reducing sulphate as the other organic substrates. In treatment 1, peat was reduced from 1420 to 1170 mg/L, while in treatment 2, concentrations decreased from 1420 to 1320 mg/L.

Sulphate values in treatment 3 (Fig. 3.8c) increased for all media. The increase in sulphate concentrations for treatments containing horse manure, cow manure and composted straw occurred between 4 and 8 weeks. No apparent change in sulphate concentration was observed after week 12 for horse manure and composted straw. Cow manure decreased significantly at week 12, but increased for the duration of the experiment. Sulphate concentrations for peat were relatively stable throughout the experiment with the exception of a decrease at week 8.

Chloride: In IC analysis, multiple peaks were encountered at the chloride attention time that could not be separated for some samples. This was likely due to the sample matrices and, therefore, chloride concentrations were not calculated for treatment 3, treatments 1 and 2 at week 12, or treatment 1 for peat at week 8. Concentrations for treatment 1 (Fig. 3.9a) and treatment 2 (Fig. 9b) were similar for horse manure, wood chips and peat, with all undergoing a slight in chloride. Concentrations for cow manure in both experiments increased at week 4, but for subsequent weeks the concentration of chloride was below the minimum detection limit.

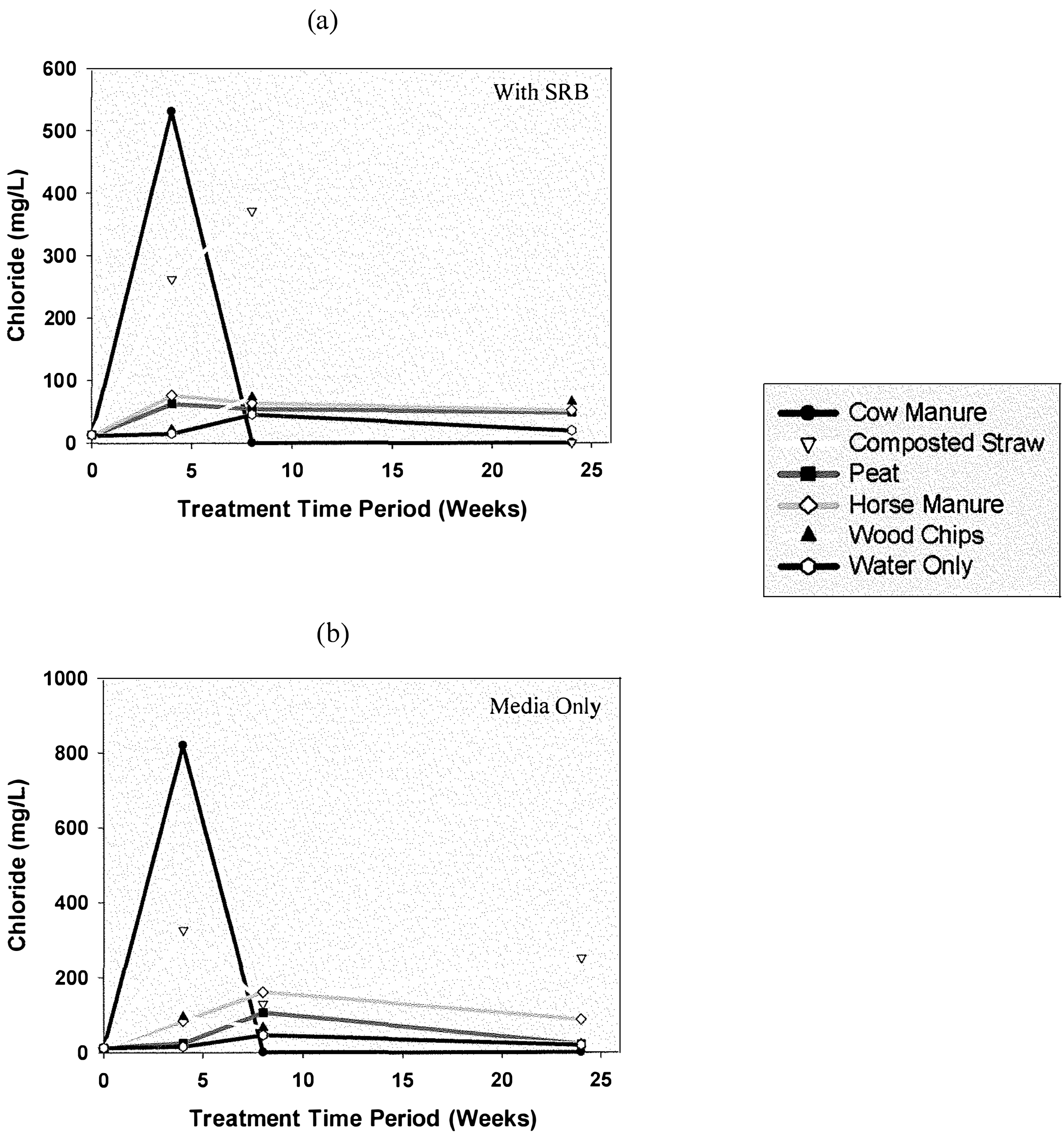


Figure 3.9: Variation in chloride content of batch reactor waters over the duration of the experiment. (a) Treatment 1 includes the addition of a SRB source to the reactive media. (b) Treatment 2 (reactive media only). Analytical uncertainty (+/- 2.1) is less than the symbol size.

Chloride concentrations for composted straw in treatment 1 increased for the first 8 weeks, but decreased for the rest of the experiment, whereas treatment 2 concentrations increased at week 4, decreased at week 8 and showed a slight increase until week 24. Concentrations for water-only remained relatively stable in all treatments.

Sulphide: The concentration of sulphide for cow manure exhibited similar trends for treatment 1 (Fig. 3.10a) and treatment 2 (Fig. 3.10b). Both treatments resulted in an increase in sulphide concentration by week 4 (0.46 mg/L for treatment 1 and 0.97 mg/L for treatment 2). By week 8 concentrations were below detection, but variably increased in both treatments over the subsequent weeks. The sulphide concentration for water treated with wood chips, peat and horse manure remained below the detection limit for treatment 1 throughout the experiment, excluding a recorded concentration of 0.16 mg/L at week 12 for horse manure. Concentrations for composted straw in treatment 1 remained below detection with the exception of recorded concentrations of 0.28 mg/L at week 4 and 0.40 mg/L at week 12. Concentrations for peat and horse manure remained below detection for treatment 2 with the exception of recorded concentrations of 0.2 mg/L at week 4 for peat, and 0.14 mg/L at week 4 and 0.2 mg/L at week 8 for horse manure, respectively. Concentrations for composted straw for treatment 2 were below detection up to week 4, but increased to 0.23 mg/L at week 12, and decreased to below detection at week 24. Wood chips in treatment 2 exhibited the most variable trends with an increase at week 4 to 0.4 mg/L, a decrease to below detection at week 8 and an increase to 0.42 mg/L between weeks 8 and 24. No data was available for treatment 3 because the water with molasses was too viscous and turbid for the spectrophotometer analysis. The concentration of sulphide in the control water remained stable for all treatments.

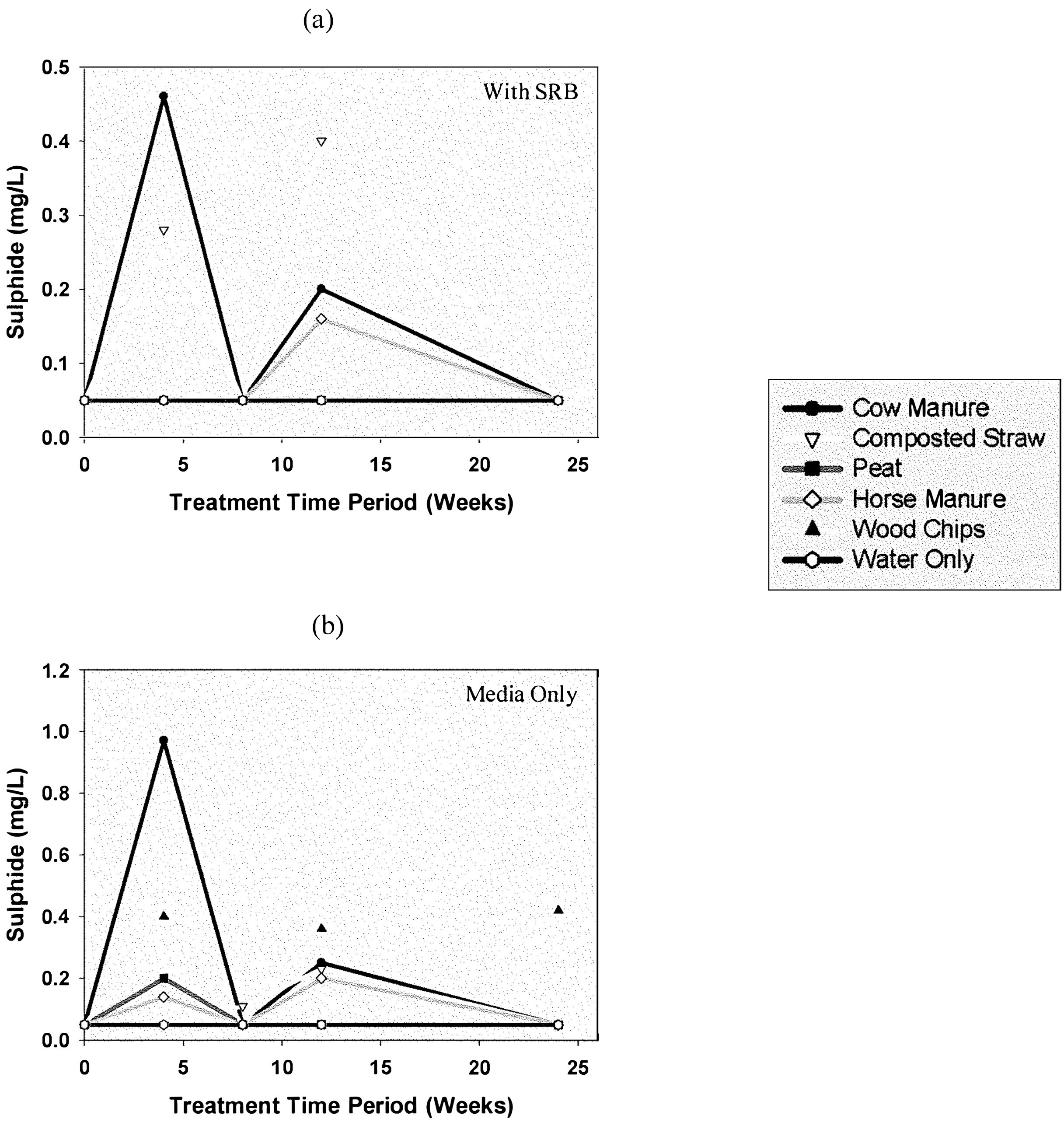


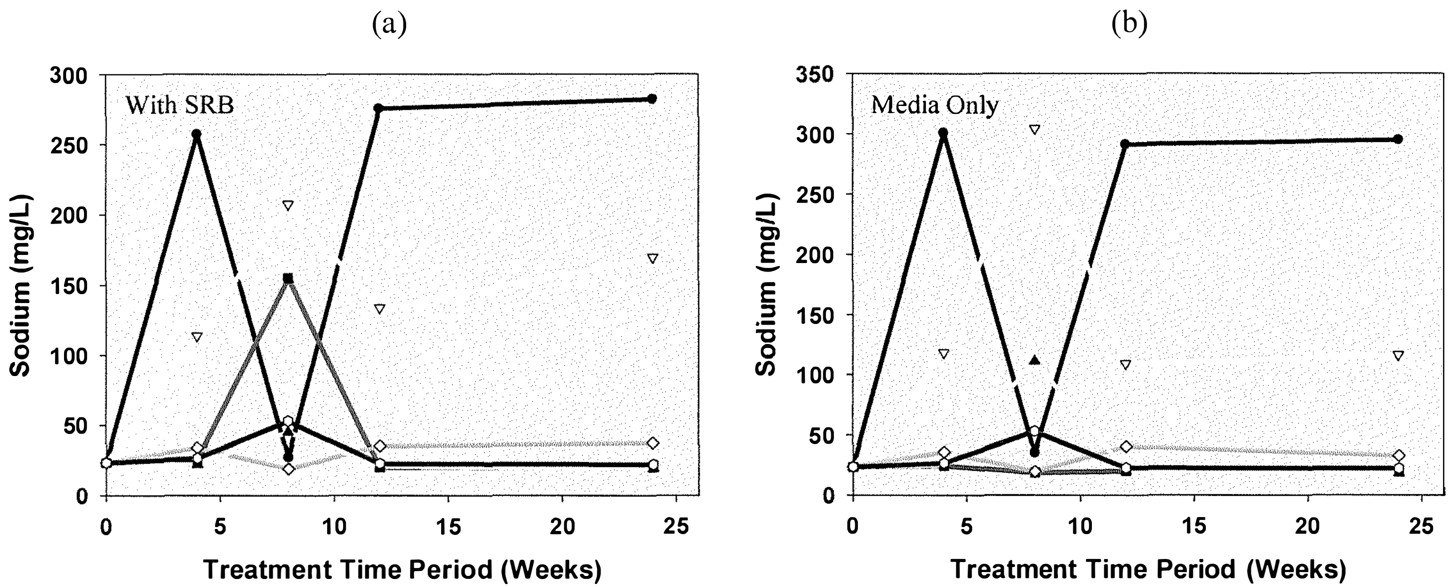
Figure 3.10: Variation in the sulphide content of batch reactor waters over the duration of the experiment. (a) Treatment 1 includes the addition of a SRB source to the reactive media. (b) Treatment 2 (reactive media only). Analytical uncertainty (+/- 0.01) is less than the symbol size.

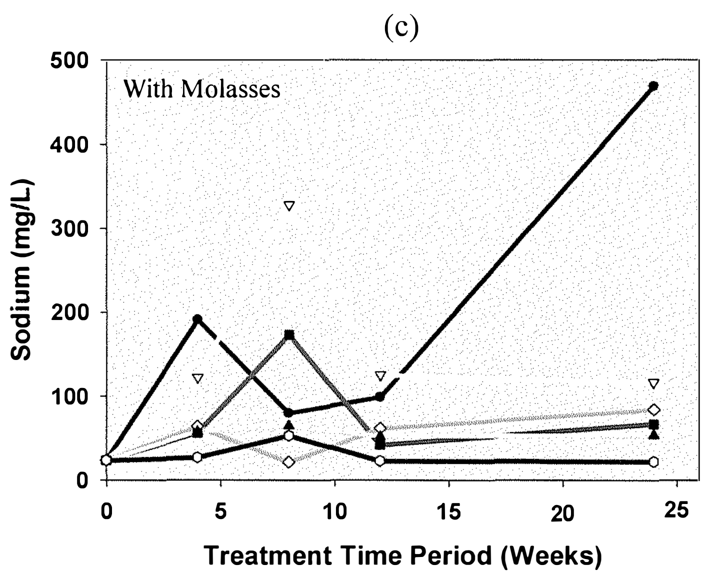
treatment 2 concentrations at week 24 were 374 mg/L and 298 mg/L for cow manure and composted straw, respectively.

3.2.4 Major Cations

Sodium: The variation in concentration of sodium was similar for all treatments (Figs. 3.11a; 3.11b; 3.11c). Concentrations for cow manure showed an initial increase at week 4, decreased between weeks 4 and 8, before increasing to >300 mg/L at week 24. Treatment 3 had the greatest increase for cow manure to 469 mg/L. Concentrations for composted straw showed an initial increase to week 8 and a decrease at week 12 in all treatments; however, concentrations remained relatively stable at 116 mg/L in treatments 2 and 3, whereas concentrations increased slightly to 170 mg/L in treatment 1. Concentrations for peat, horse manure and wood chips remained relatively stable throughout the experiment in all treatments, with a few exceptions. Concentrations in treatment 3 and concentrations for horse manure in treatments 1 and 2 showed a slight increase throughout the experiment. Also, the value for wood chips in treatment 2 and peat in treatments 1 and 3 exhibited slight increases between weeks 4 and 9, although no other changes were observed.

Potassium: Potassium concentrations for treatment 1 (Fig. 3.12a) and treatment 2 (Fig. 3.12b) showed similar trends. An increase throughout the experiment was observed for cow manure, composted straw and horse manure in both treatments. Cow manure had the greatest increase (>1200 mg/L), followed by composted straw (>600 mg/L) and horse manure (>300 mg/L). Wood chips and peat remained relatively stable throughout the experiment in treatments 1 and 2. Treatment 3 (Fig. 3.12c) potassium concentrations generally had the greatest increase, more than twice the concentrations of the other treatments. Concentrations for cow manure, composted straw, horse manure and peat followed a similar trend with an initial increase until week 8, a





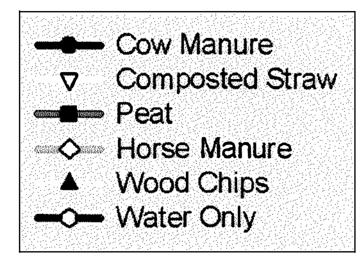
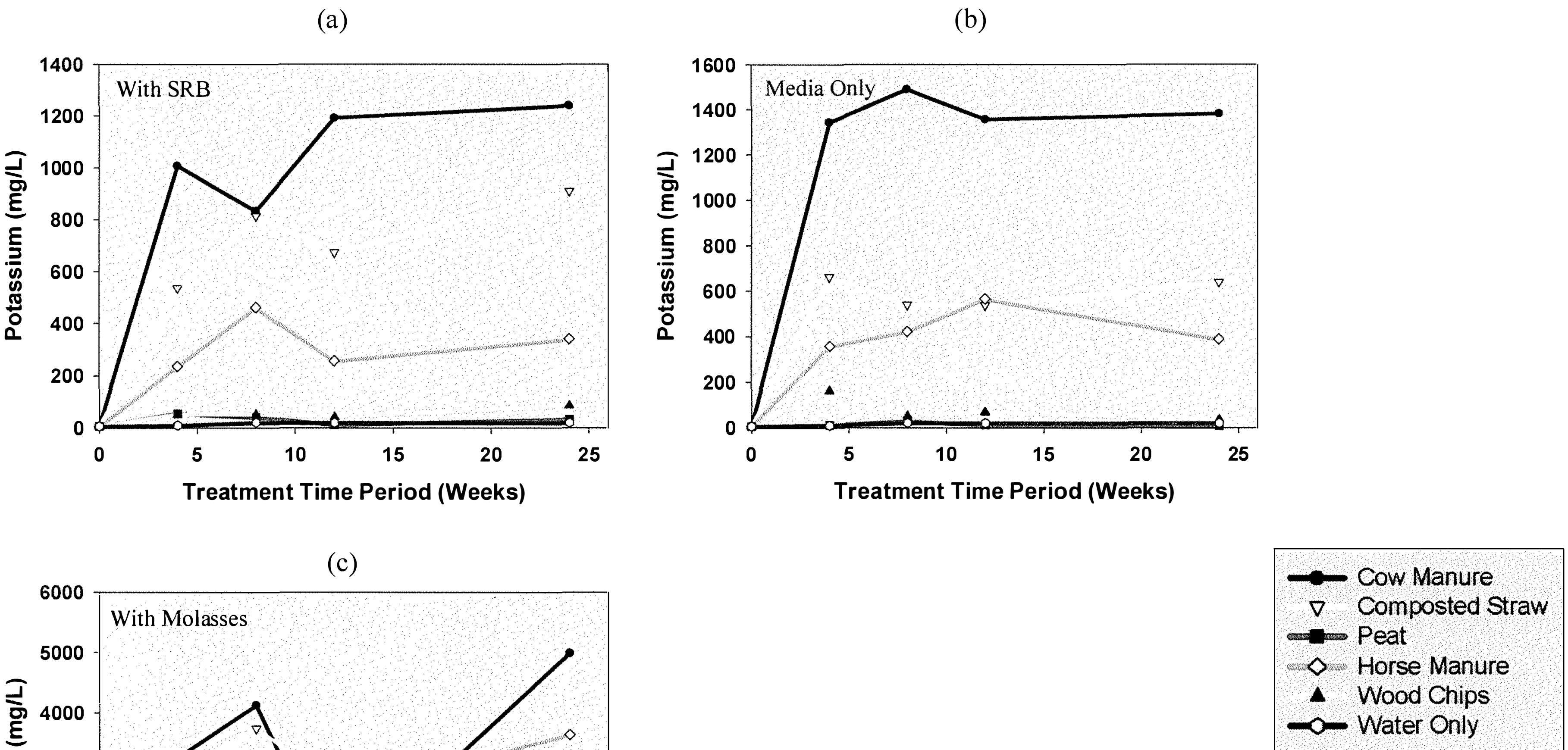


Figure 3.11: Variation in the sodium content of batch reactor waters over the duration of the experiment. (a) Treatment 1, which includes the addition of a SRB source to the reactive media. (b) Treatment 2 (reactive media only). (c) Treatment 3, which includes the addition of molasses to the reactive media. Analytical uncertainty (+/- 2.1) is less than symbol size.



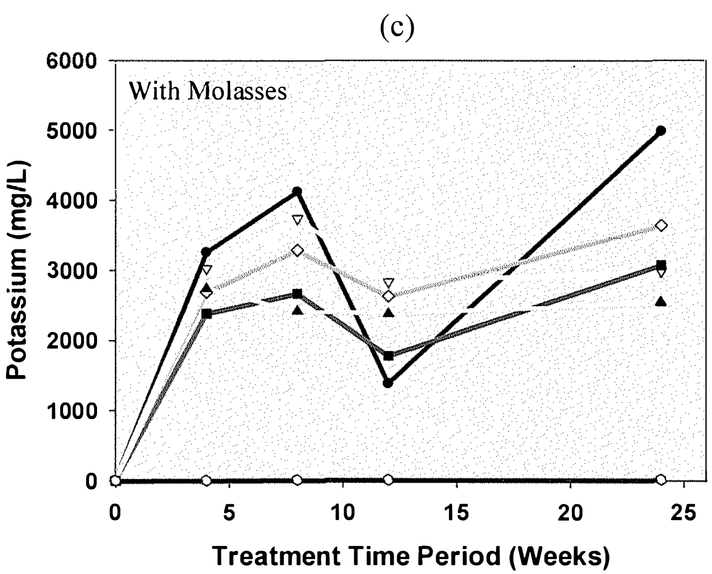


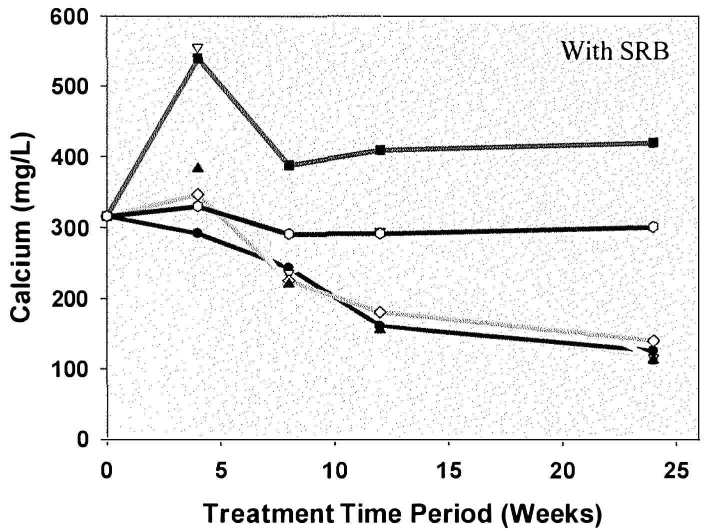
Figure 3.12: Variation in the potassium content of batch reactor waters over the duration of the experiment. (a) Treatment 1, which includes the addition of a SRB source to the reactive media. (b) Treatment 2 (reactive media only). (c) Treatment 3, which includes the addition of molasses to the reactive media. Analytical uncertainty (+/- 5.2) is less than symbol size.

decrease between weeks 8 and 12 and an increase for the duration of the experiment. Cow manure had the greatest overall increase from 6.5 to 5000 mg/L. Wood chips showed an initial increase at week 4, but remained relatively stable between 4 and 24 weeks. Wood chips also had the highest increase, which was from 6.5 mg/L to 2540 mg/L. Concentrations for water-only remained similar to initial values in all treatments.

Calcium: The concentration of calcium for horse manure, wood chips and cow manure in both treatment 1 (Fig. 3.13a and treatment 2 (Fig. 3.13b), and composted straw (treatment 1 only) generally decreased throughout the experiment to approximately 120 mg/L at week 24. Treatment 2 concentrations for composted straw initially increased up to week 4, but decreased to 293 mg/L by week 24. Calcium concentrations for both treatment 1 and 2 with peat were variable throughout weeks 1 to 8, but stabilized for the remainder of the experiment. Treatment 3 (Fig. 3.13c) had the greatest change, with each of the reactive media producing significant increases in calcium concentrations (>2000 mg/L). All of the organic matter also had initial increases in calcium at week 4, and concentrations decreased between weeks 4 and 12, but increased for the remainder of the experiment. Concentrations for water-only in all treatments remained stable throughout the experiment.

Magnesium: The changes in magnesium concentrations for both treatment 1 (Fig. 3.14a) and treatment 2 (Fig. 3.14b) exhibited similar trends throughout the experiment. Concentrations for composted straw in both treatments increased up to 4 weeks and decreased at 8 weeks to approximately 180 mg/L; however treatment 1 remained relatively stable throughout the rest of the experiment, whereas treatment 2 increased to 218 mg/L between 8 and 24 weeks. Concentrations for cow manure and horse manure in both treatments remained relatively stable throughout the experiment, with the exception of a slight increase for cow manure in treatment 1 and a slight decrease for horse manure in both treatments. Concentrations for wood chips and

(a)



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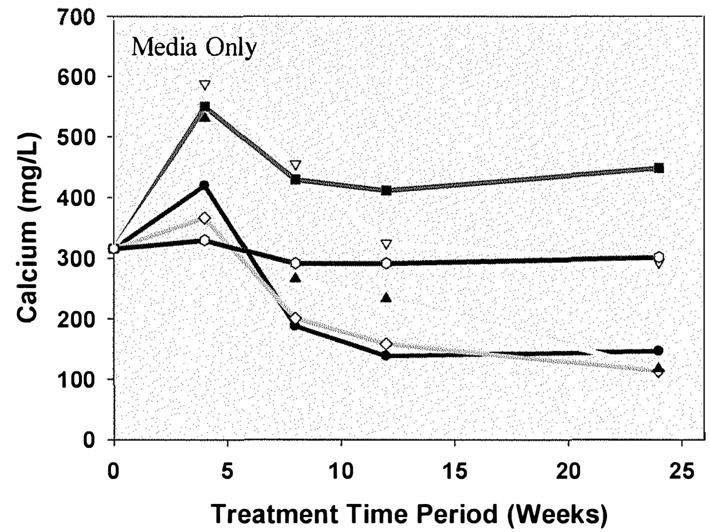

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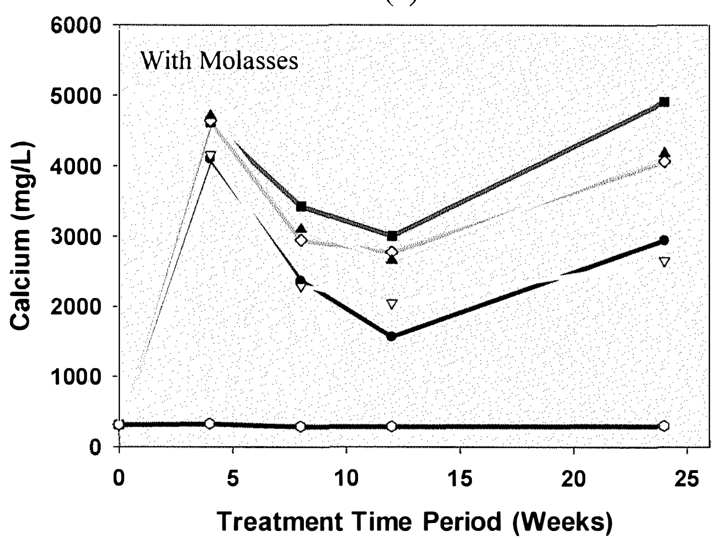


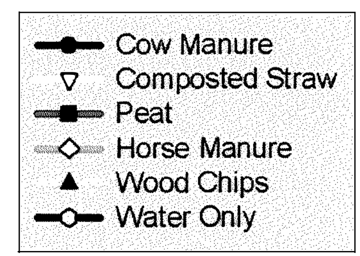


Figure 3.13: Variation in the calcium content of batch reactor waters over the duration of the experiment. (a) Treatment 1, which includes the addition of a SRB source to the reactive media. (b) Treatment 2 (reactive media only). (c) Treatment 3, which includes the addition of molasses to the reactive media. Analytical uncertainty (+/- 16.8) is less than symbol size

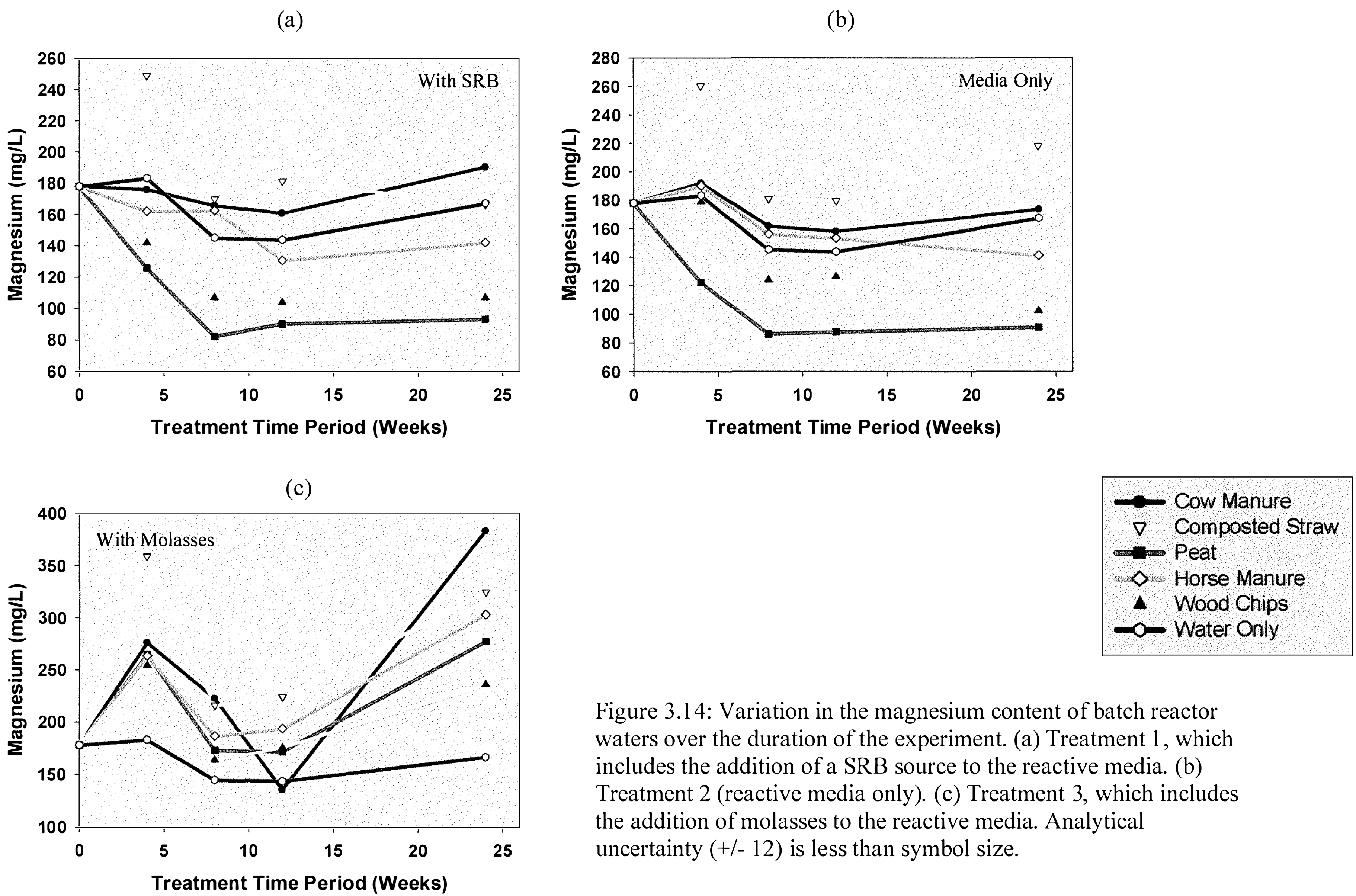


Figure 3.14: Variation in the magnesium content of batch reactor waters over the duration of the experiment. (a) Treatment 1, which includes the addition of a SRB source to the reactive media. (b) Treatment 2 (reactive media only). (c) Treatment 3, which includes the addition of molasses to the reactive media. Analytical uncertainty (+/- 12) is less than symbol size.

peat showed decreasing trends in both experiments, with wood chips decreasing to approximately 105 mg/L and peat decreasing to approximately 90 mg/L at 24 weeks for both treatments. Treatment 3 (Fig. 3.14c) concentrations showed an overall increase in magnesium. Each of the organic materials showed an initial increase up to week 4, decreased between weeks 4 and 8, and increased for the remainder of the experiment. Cow manure had the highest increase in magnesium from 276 mg/L to 383 mg/L.

Iron and other metals: Iron concentrations were similar in treatment 1 (Fig. 3.15a) and treatment 2 (Fig. 3.15b). All reactive media showed an overall increase, but different trends were observed in each. Concentrations for other metals (vanadium, chromium, manganese, cobalt, nickel, copper, barium, cadmium, lead, aluminum and zinc), were generally below the laboratory detection limit, or followed a similar trend to iron in all treatments. Iron values for horse manure showed the greatest increase in treatment 1, with concentrations reaching around 40 mg/L at week 24, whereas concentrations for cow manure showed the greatest increase in treatment 2 to approximately 50 mg/L. Iron values for wood chips showed an increase at week 4 to approximately 90 mg/L, decreased at week 4, and increased between weeks 12 and 24 in treatment 1. Peat, cow manure and composted straw iron concentrations in both treatments showed an increase to approximately 20 mg/L throughout the experiment. Treatment 3 (Fig. 3.15c) had the highest iron concentrations of the three treatments. All of the iron concentrations in the reactive media had an initial increase at 4 weeks. Iron concentrations in horse manure, cow manure and composted straw decreased between 4 and 12 weeks, and peat and wood chips decreased between 4 and 8 weeks, before increasing for the duration of the experiment. All iron values increased to >600 mg/L with peat exhibiting the largest increase (>1090 mg/L). Concentrations for water-only remained relatively stable in all treatments.

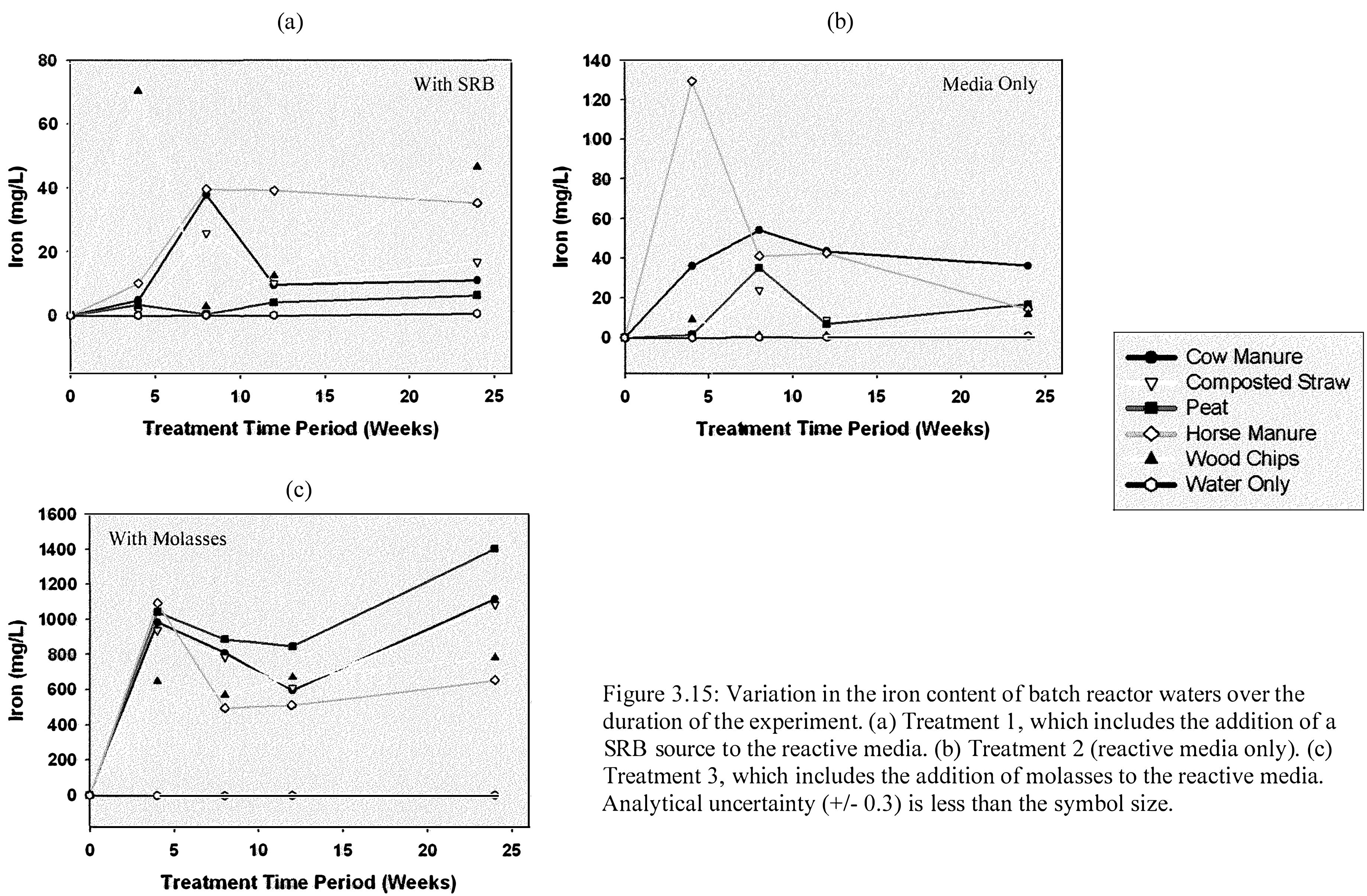


Figure 3.15: Variation in the iron content of batch reactor waters over the duration of the experiment. (a) Treatment 1, which includes the addition of a SRB source to the reactive media. (b) Treatment 2 (reactive media only). (c) Treatment 3, which includes the addition of molasses to the reactive media. Analytical uncertainty (+/- 0.3) is less than the symbol size.

3.3 Results for Flow-through Reactor Experiments

The final water composition of the flow-through reactors is provided in Table 3.9. During the experiment, no concentrations were obtained for reactors 2, 6 and 8 at the week 20 sampling period due to a shortage in water volume resulting from clogging of the reactors. Time series graphs for flow-through reactors and results for week 16 of the flow-through reactor columns are shown below. The complete compositional data set for flow-through reactor waters is provided in Appendix 4.

Table 3.9: Final water chemistry compositions (week 16) for flow-through reactor experiments.

Treatment	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Reactor 5	Reactor 6	Reactor 7	Reactor 8
Conductivity (µs/cm)	2350	2280	2540	2160	2190	2420	2390	2130
TDS	1150	1120	1250	1060	1070	1190	1170	1040
Aluminum	0.06	0.05	0.08	0.05	0.04	0.04	0.08	0.09
Arsenic	0.02	0.03	0.02	0.01	0.02	0.02	0.02	0.02
Barium	0.13	0.10	0.09	0.10	0.12	0.10	0.11	0.12
Berrylium	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Calcium	280	269	232	270	250	276	267	247
Manganese	0.72	0.70	0.52	0.53	0.70	0.60	0.53	0.61
Sodium	23.6	22.8	19.4	22.8	20.9	23.5	22.4	20.6
Nickel	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Vanadium	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Zinc	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.02
Lead	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Sulphur	379	386	312	359	340	398	359	324
Potassium	17.1	8.70	157	6.10	9.30	6.60	6.40	5.50
Chromium	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Iron	0.09	0.06	0.16	0.05	0.09	0.03	0.04	0.04
Cobalt	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
pH	8.02	8.40	7.73	8.30	8.28	7.71	7.67	8.27
Chloride	24.8	19.3	0.03	15.3	18.1	16.2	16.3	13.7
Sulphide	8.24	5.92	N	9.76	2.40	6.40	2.72	5.36
Redox (mV)	-259	-288	-295	-287	-264	-297	-280	-26
Bicarbonate	383	323	N	409	381	352	419	382
Alkalinity (as $CaCO_3$)	387	331	N	417	389	354	421	390
Sulphate	1130	1210	N	1090	1080	1240	1160	1030

Results are shown in mg/L, unless otherwise stated. Results for week 20 are not shown because no data was available for reactors 2, 6 and 8. Values with N indicate that there was not enough water to take a sample.

3.3.1 Initial Residence Time

The residence time is the time that water remains in the flow-through reactor and corresponds to the time that the same water reacts within the reactive media. This was calculated by determining the amount of time to initially fill a reactor at an average linear velocity of 0.1 mL/min. Residence times were only determined at the beginning of the experiment, and the approximate residence times of each flow-through reactor are listed below (Table 3.10):

Table 3.10: Initial residence time for flow-through reactors

Reactor No.	Residence Time
Reactor 1	71 hrs 40 mins
Reactor 5	127 hrs 35 mins
Reactor 2	91 hrs 50 min
Reactor 6	92 hrs 30 mins
Reactor 3	70 hrs 10 mins
Reactor 7	74 hrs 20 mins
Reactor 4	130 hrs 20 mins
Reactor 8	94 hrs 15 mins

Reactor 4 had the longest residence time of 130 hours and 20 minutes, while reactor 1 had the shortest residence time of 71 hours and 40 minutes. Residence times are different between the reactors with the same reactive media due to differences in permeability, which likely reflect differences in the degree of compaction during loading.

3.3.2 Physical Water Quality Parameters

pH: The initial pH value for the stock water was 7.9, and an initial decrease of about 1.5 was observed for the first two weeks of the experiment in each of the reactors, including the initial water (Fig. 3.16a). After this time, the values began to steadily increase for the next 10-12 weeks. At week 13 the majority of the reactors were between 8.2 and 8.3, with the exception of reactor 1 which had a pH value of 8.1. After week 13, reactor 1 decreased to 7.4, increased to 8.1 at week 15 and decreased to 7.3 at the end of the experiment. The rest of the reactors showed

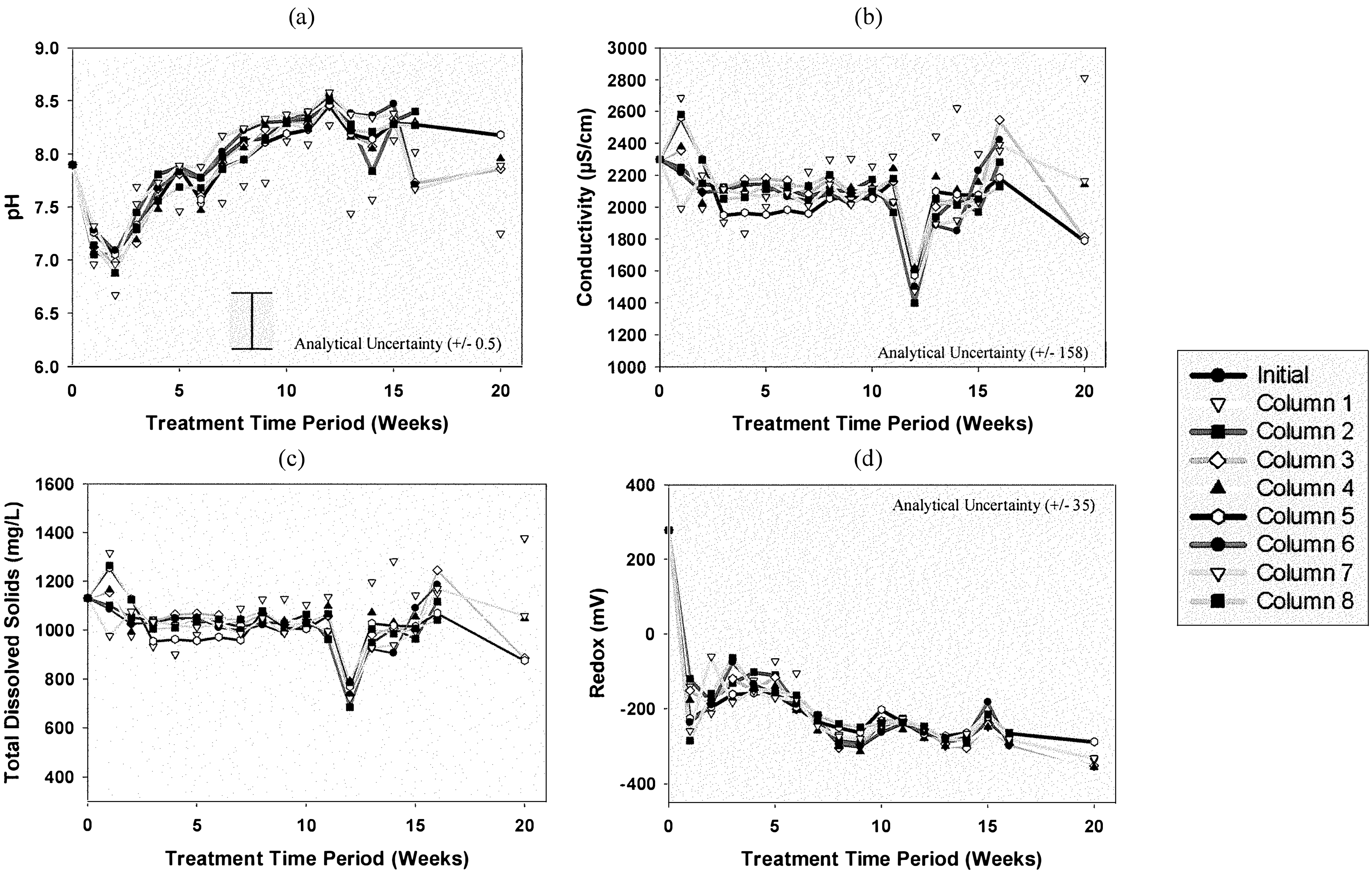


Figure 3.16: Variation in (a) pH, (b) conductivity, (c) TDS and (d) redox for the flow-through experiments. Reactors1 and 5 are two reaction chambers separated by silica sand; reactors 2 and 6 are two reaction chambers separated by carbonate rock; reactors 3 and 7 are three reaction chambers separated by silica sand; and, reactors 4 and 8 are one reaction chamber.

Similar trends throughout the first 16 weeks of the experiment, with a general decrease after between 16 and 20 weeks.

Conductivity and Total Dissolved Solids: Conductivity (Fig. 3.16b) and TDS (Fig. 3.16c) trends were very similar throughout the experiment. The initial value for conductivity was 2301 μS/cm and 1132 mg/L for TDS. Reactors 1, 5 and 8 each exhibited an overall increase in conductivity and TDS to approximately 2600 μS/cm and 1300 mg/L, respectively, whereas reactor 7 decreased to 1992 μS/cm and 976 mg/L, respectively. Each of the reactors showed an initial decrease to around 2100 μS/cm for conductivity and 1000 mg/L for TDS, and remained steady around this value for the first 15 weeks of the experiment. However, there was a significant decrease in all conductivity and TDS values to around 1500 μS/cm and 700 mg/L for TDS, respectively, at week 12. Reactor 1 showed the greatest variation in conductivity values. After the initial increase, the value decreased to below the values for all other reactors for the first 5 weeks of the experiment and then steadily increased above other reactor values for the remainder of the experiment. After 16 weeks, reactors 2, 3, 6 and 7 increased significantly, but reactors 3 and 7 had decreased again after 20 weeks (no data for reactors 2 and 6).

Reduction-Oxidation Potential (Redox): Redox values exhibited a significant decrease after week 1 of the experiment (Fig. 3.16d). The initial redox value for the 18 m Hogarth pit lake water was 278.7 mV and all values decreased to less than -100 mV. The highest decrease was in reactor 8 (-283.9 mV). Generally, redox values increased between weeks 1 and 5 and there was a decrease for the remainder of the experiment. At weeks 16 and 20, all values were approaching -300 mV.

3.3.3 Major Anions

Total Alkalinity (as $CaCO_3$) and Bicarbonate: Each of the alkalinity (Fig. 3.17a) and bicarbonate (Fig.3.17b) values in the eight flow-through reactors exhibited an initial increase of about 250 mg/L to between 400 and 500 mg/L after the first week. Reactor 5 showed a higher increase at this time and remained higher than the others for the first 12 weeks of the experiment. A steady increase in alkalinity was observed for most of the reactors between weeks 1 and 12, after which concentrations become relatively stable around 400 mg/L for the remainder of the experiment. Reactor 1 and reactor 5 had higher alkalinity during the first 12 weeks of the experiment, especially reactor 1, but increased to 1343 mg/L at week 3, but declined steadily until week 10, matching values similar to the other reactors. There was no alkalinity data available during week 7 due to shortage of water in the reactor.

Sulphate: The stock water had an initial sulphate value of 1590 mg/L (Fig. 3.17c). The concentration of sulphate decreased in all reactors over the first 3-6 weeks, before increasing slightly for the remainder of the experiment. Reactor 1 displayed the most pronounced decrease in sulphate levels which occurred during week 4 at 201 mg/L and corresponds to an 87% decrease. The sulphate concentrations for reactor 1 increased in subsequent weeks, but were also below initial concentrations. Reactor 5 also had a greater decrease than the other reactors, with a value of 442 mg/L at week 3 (72% decrease). Reactor 5 sulphate values remained below the average value for the first 10 weeks, before following a similar trend to the rest of the reactors and increasing slightly for the remainder of the experiment. On average, the most successful sulphate reduction occurred between weeks 3 and 8, where concentrations were consistently below 900 mg/L (>44% average decrease). The best average week during this time was week 2 with a value of 720 mg/L (55% average decrease). Average values remained below 1000 mg/L (37% average decrease) until week 15. By week 16 of the experiment, values had begun to

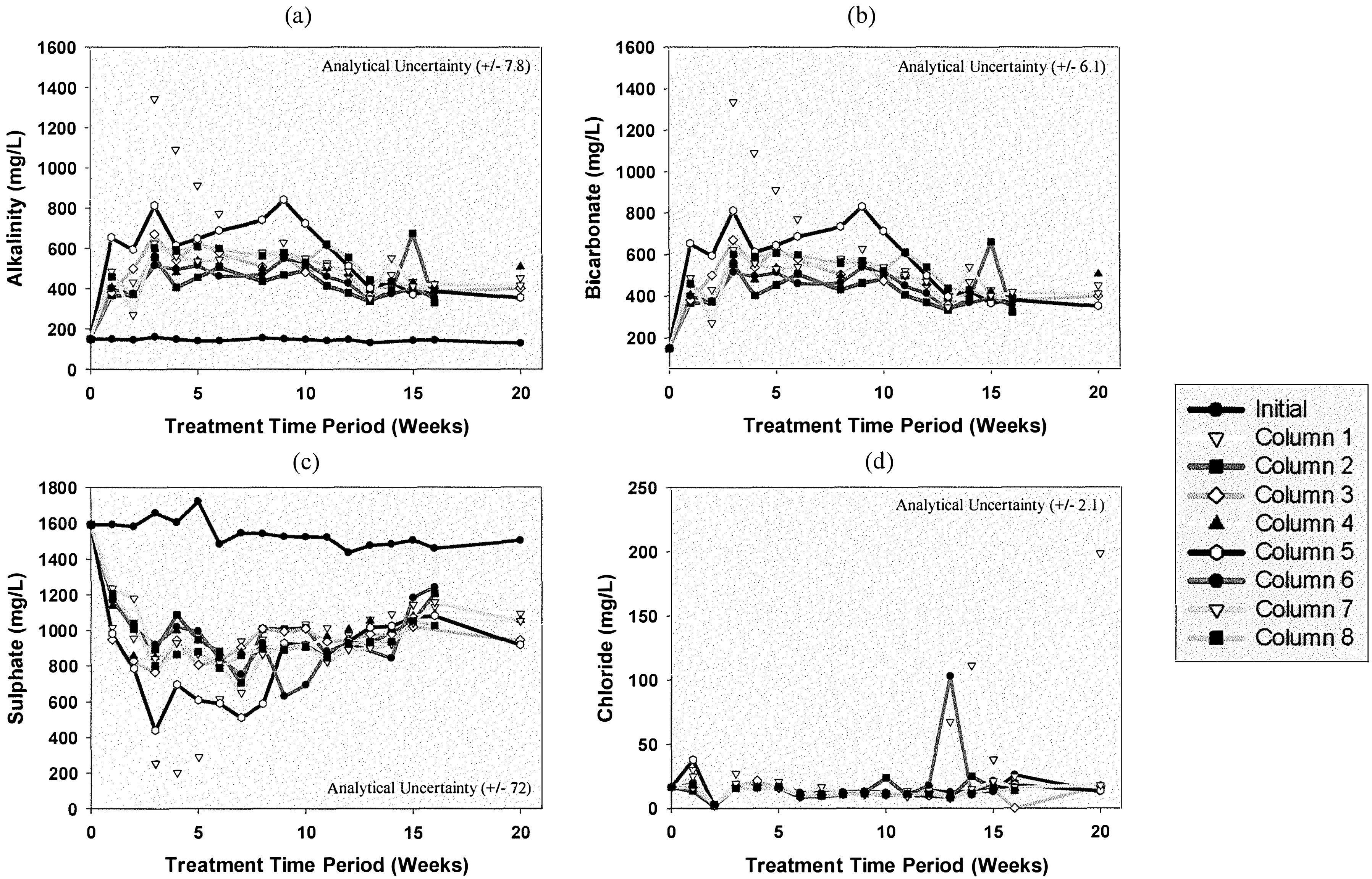


Figure 3.17: Variations in (a) alkalinity (b) bicarbonate (c) sulphate and (d) chloride. Reactors1 and 5 are two reaction chambers separated by silica sand; reactors 2 and 6 are two reaction chambers separated by carbonate rock; reactors 3 and 7 are three reaction chambers separated by silica sand; and, reactors 4 and 8 are one reaction chamber.

increase steadily, but the average value of 1130 mg/L (29% average decrease) was still well below the initial concentrations.

The most successful period of sulphate reduction in this experiment occurred between weeks 3 and 8 in all reactors, with average decreases in sulphate values > 42%. At this time, reactor 1 showed the highest decrease in sulphate with an average reduction of 84.3%.

Chloride: Chloride concentrations experienced a decrease at week 3 in all reactors (Fig. 3.17d), but remained relatively stable throughout the entire experiment with a few exceptions. First, reactors 5 and 7 had a small increase after 1 week, but achieved a steady state for the duration of the experiment. Reactor 1 had a small increase at week 1 as well, but also had a large increase during weeks 13 and 14, decreased during weeks 15 and 16 and had a dramatic increase at week 20. Reactor 2 had increased slightly at week 10 and reactor 6 increased at week 13. Reactor 1 also experienced a small decrease in values at week 16.

Sulphide: Sulphide concentrations were highly variable throughout the entire experiment (Fig. 3.18b). Generally, there was an initial increase from the start to between 4 and 8 mg/L in all of the reactors and it remained between 2 and 6 mg/L for the remainder of the experiment. Reactor 4 had the highest sulphide concentrations but was still highly variable from week to week. No sulphide data was available for weeks 3, 4, 5 due to an issue with laboratory equipment, and no data was available for week 20 due to water volume issues.

Since sulphide values were variable throughout the experiment, titration may not be the most accurate method to determine sulphide values. Other analyses, such as the methylene blue method by UV mass spectrophotometry used by Gilbert et al. (2004) may attain more accurate values.

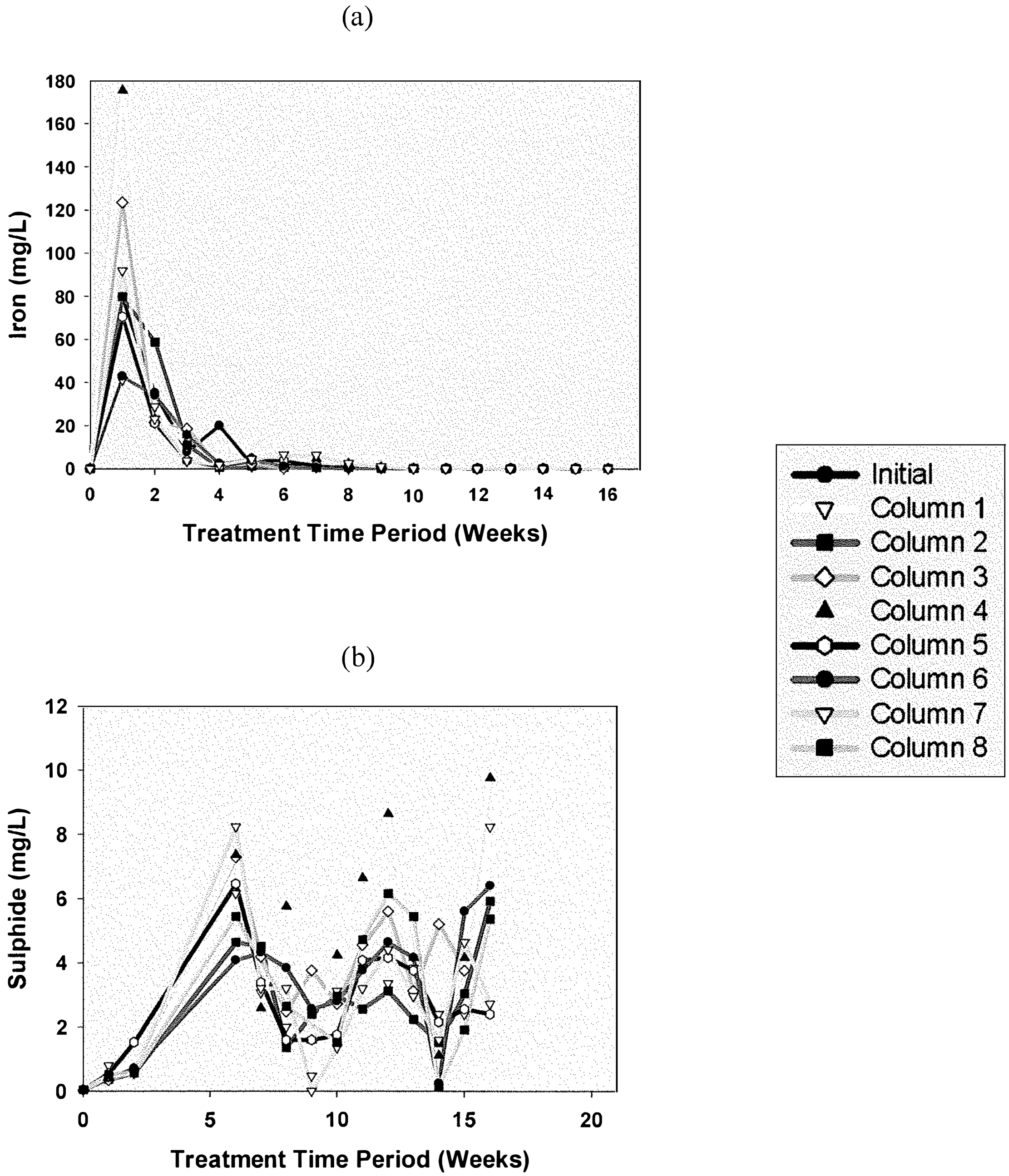


Figure 3.18: Variations in (a) iron and (b) sulphide for flow-through experiments. Reactors1 and 5 are two reaction chambers separated by silica sand; reactors 2 and 6 are two reaction chambers separated by carbonate rock; reactors 3 and 7 are three reaction chambers separated by silica sand; and, reactors 4 and 8 are one reaction chamber. Analytical uncertainties for iron (+/- 0.01) and sulphide (+/- 0.01) are smaller than symbol size.

3.3.4 Major Cations

Calcium: The initial calcium value for the stock water was 320 mg/L (Fig. 3.19a). Calcium concentrations were highly variable for the duration of the experiment. Concentrations decreased for the first 2 weeks of the experiment in each of the reactors. A slight increase was observed between weeks 2 and 12. Most reactors begin to decrease again after week 12, with the exception of reactors 2 and 6. Both reactors increased between weeks 2 and 10 followed by a decrease between weeks 10 and 13, but increased for the remainder of the experiment. Calcium concentrations remained below initial levels in all reactors for the duration of the experiment.

Magnesium: Magnesium exhibited almost identical trends to the concentrations for calcium. The initial magnesium value was 173 mg/L (Fig. 3.19b). In general, values decreased for the first 2 weeks of the experiment, increased between weeks 2 and 12, and began to decrease for the remainder of the experiment. Reactors 2, 6 and 7 were the exceptions, with concentrations decreasing between weeks 10 and 13 and then increasing for the remainder of the experiment. Magnesium remained below initial concentrations in all reactors for the duration of the experiment.

Sodium: The initial sodium value for the stock water was 23.6 mg/L (Fig. 3.19c). Reactors 1, 4, 5, 6 and 7 all showed increases for the first week of the experiment, with reactor 5 having the highest increase to 36.8 mg/L. Generally, each of the reactors had decreased to below initial concentrations by week 3, increased between weeks 3 and 5, and exhibited a minor decrease between weeks 5 and 15. Reactors 1, 3, 6 and 7 had an increase in value between weeks 15 and 20.

Potassium: The initial potassium value in the stock water was 6.80 mg/L (Fig. 3.19d). Generally, potassium concentrations increased initially in all reactors in the first week of the

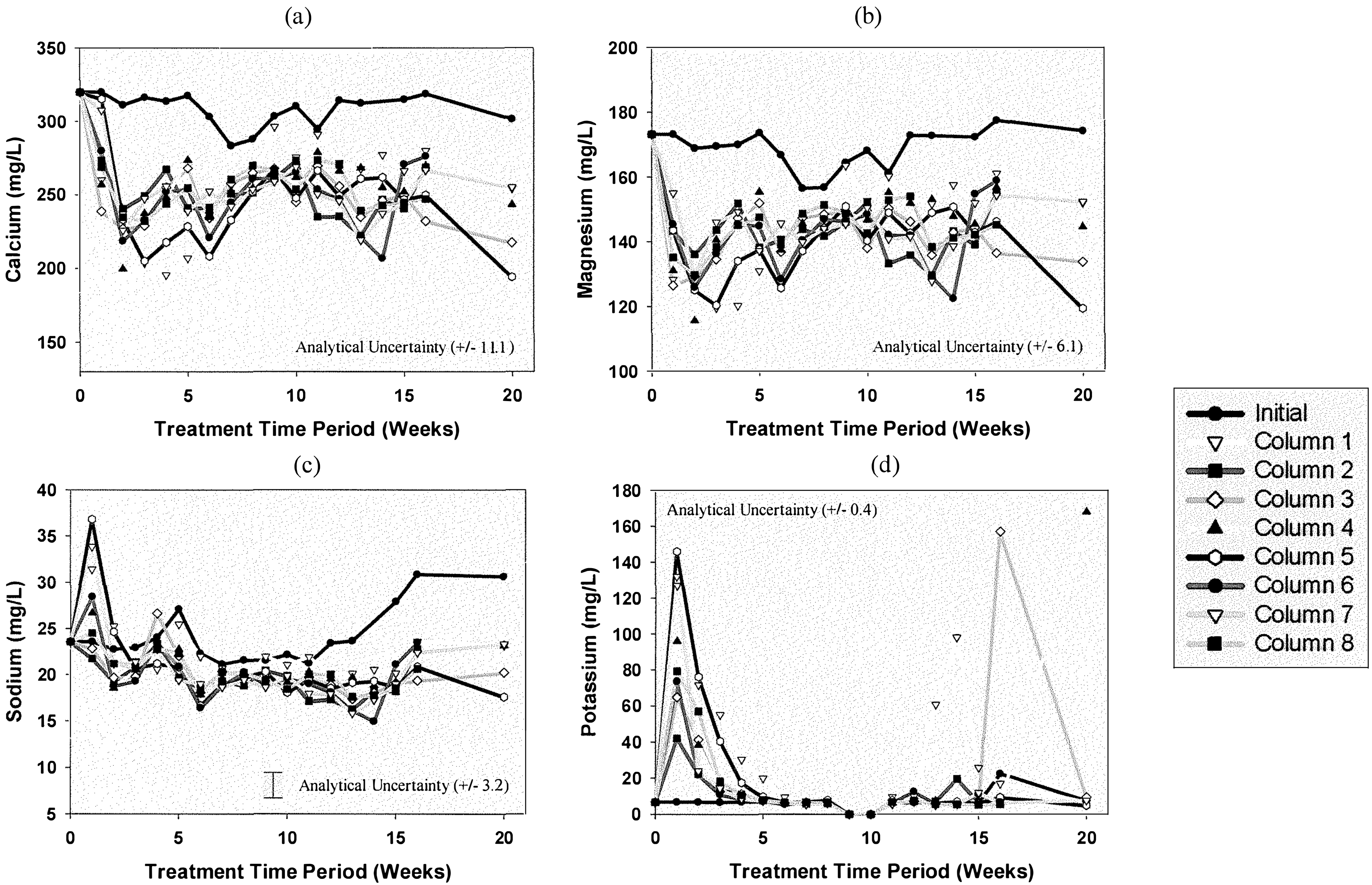


Figure 3.19: Variations in (a) calcium (b) magnesium (c) sodium and (d) potassium for the flow-through experiments. Reactors1 and 5 are two reaction chambers separated by silica sand; reactors 2 and 6 are two reaction chambers separated by carbonate rock; reactors 3 and 7 are three reaction chambers separated by silica sand; and, reactors 4 and 8 are one reaction chamber.

experiment, followed by a decrease to initial concentrations by week 5. Reactor 5 had the highest initial increase to 146.0 mg/L. Both reactor 1 (7 weeks) and reactor 5 (6 weeks) took longer than the other reactors to return to initial stock water concentrations. Reactor 1 showed an increase spike between week 12 and week 15, but decreased to initial concentrations by the end of the experiment. Reactor 3 also had a spike at week 16, but decreased by week 20. Reactor 4 had followed the same trends as the other reactors for the first 16 weeks, but increased significantly at week 20.

Iron and other metals: Iron concentrations showed increased initially in concentration for each of the reactors (Fig. 3.18a). Concentrations for other metals (vanadium, chromium, manganese, cobalt, nickel, copper, barium, cadmium, lead, aluminum and zinc), were generally below the laboratory detection limit, or followed a similar trend to iron in all reactors. Reactor 4 had the highest increase from 0.005 mg/L to 175.4 mg/L, whereas reactor 6 had the lowest increase which was still to 41.2 mg/L. After the first week, all reactors began to decrease between week 2 and week 5 and remained near initial concentrations for the remainder of the experiment.

3.3.5 Piper Plot Diagrams

Batch Reactors: Figure 3.20 shows a comparison of water chemistry in horse manure and wood chips from week 24 of the batch experiment to water from Caland pit lake at a depth of 18 metres and regional lake water from Finlayson, Marmion and Perch lakes. After 24 weeks, horse manure produced bicarbonate- sodium- potassium- rich water, and wood chips produced bicarbonate- magnesium-enriched water.

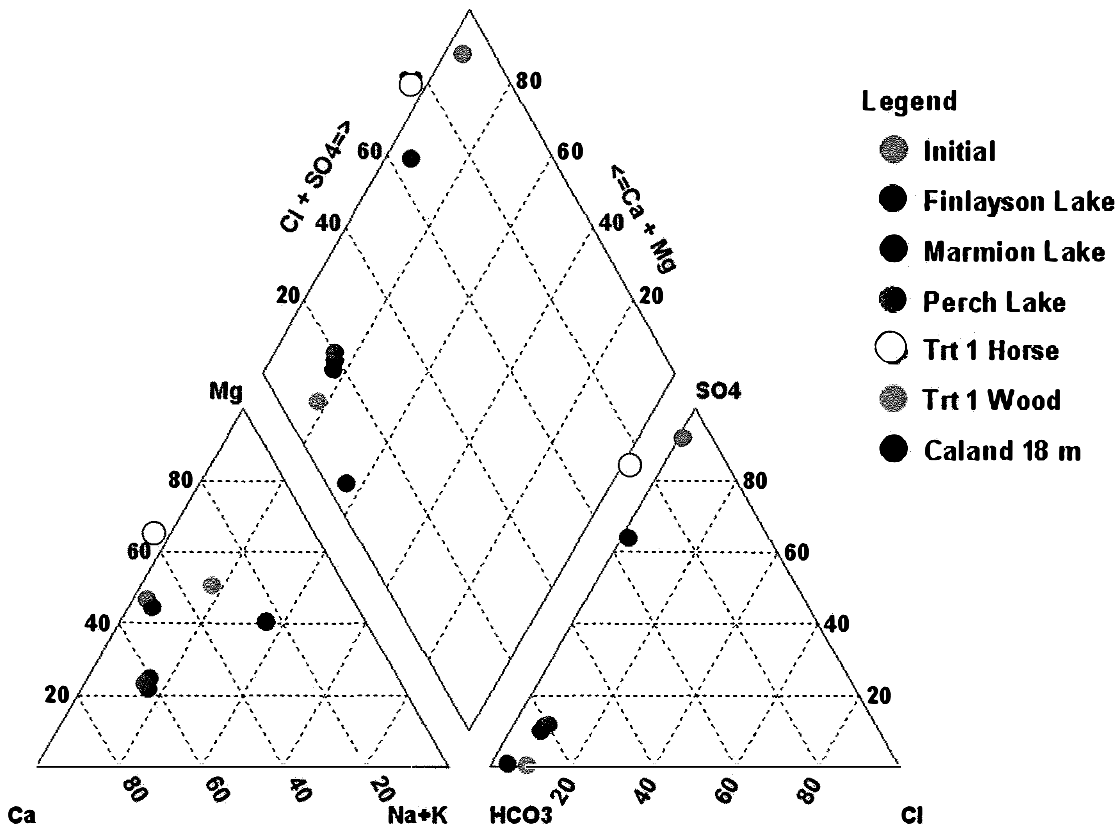


Figure 3.20: Piper diagram showing the final (24 weeks) water compositions for batch experiments using treatment 1 with horse manure and cow manure. The composition of regional water bodies (Finlayson Lake, Marmion Lake and Perch Lake) and Caland Lake (18 m water) are plotted for comparison (Caland and regional lake data courtesy of Conly and Lee, 2010, unpublished data).

Flow-Through Reactors: Piper diagrams were created to observe the evolution of anions and cations within the system. These data were plotted against Caland Lake water taken from a depth of 18 metres and regional lake water from Finlayson, Perch and Marmion lakes. In all reactors, the major cation, generally remained the same throughout the experiment (i.e., magnesium-, calcium-, dominated water), whereas anions showed a greater variation and are further discussed below.

The water in reactors 1 and 5 (Figs. 3.21a; 3.21b) were similar, and gradually became more dominated by bicarbonate within the first 4 weeks of the experiment. After week 4, the water became more sulphate-dominated. The water in reactors 2 and 6 (Fig. 3.22a; 3.22b) were similar, with anion levels beginning to move towards a more bicarbonate-dominated type in the first 3 weeks of the experiment, but by week 6, the water was between 70 and 80 mEq sulphate and remained this type for the duration of the experiment. The water in reactors 3 and 7 (Fig. 3.23a; 3.23b) were similar, with anion values moving towards a more bicarbonate dominated type in the first 6 weeks, but by week 7, they were between 60 and 80 mEq sulphate and remained this type for the duration of the experiment. The water in reactors 4 and 8 (Fig. 3.24a; 3.24b) were also similar, in which the major anion value moved towards a more bicarbonate type, but by week 7 was between 60 and 80 mEq sulphate for the duration of the experiment.

All reactors generally compared well (in terms of major anions and cations) with water from Caland Lake after 3-4 weeks of the experiment. Reactors 1 and 5 generally showed similar results between weeks 3 and 5, with reactor 1 comparing well with regional lake water during weeks 3 and 4.

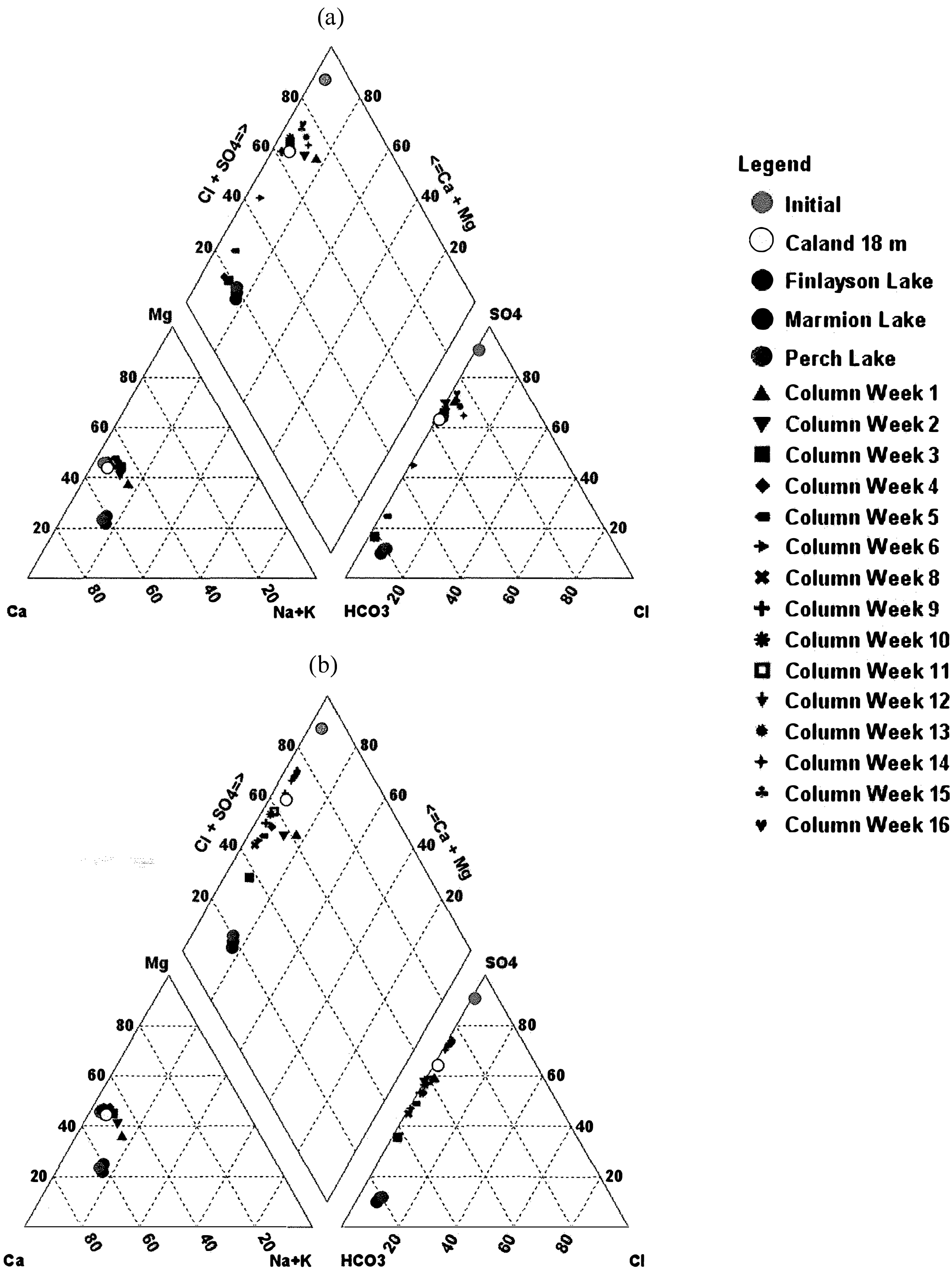


Figure 3.21: Flow-Through Reactor Piper Plot of (a) reactor 1 and (b) reactor 5. The composition of regional water bodies (Finlayson Lake, Marmion Lake and Perch Lake) and Caland Lake (18 m water) are plotted for comparison (Caland and regional water data courtesy of Conly, 2010, unpublished data).

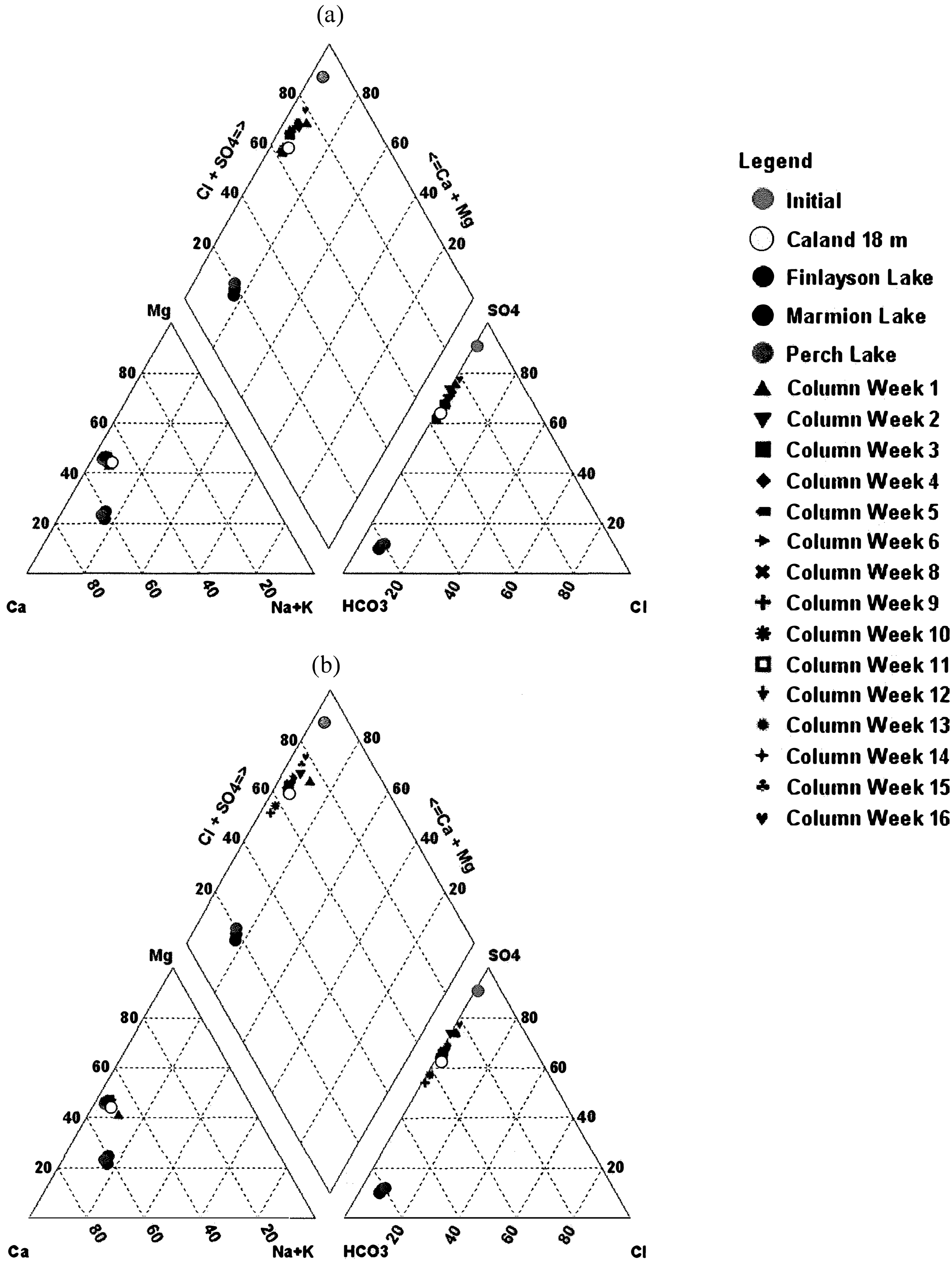


Figure 3.22: Piper diagrams for flow-through reactors (a) 2 and (b) 6. The composition of regional water bodies (Finlayson Lake, Marmion Lake and Perch Lake) and Caland Lake (18 m water) are plotted for comparison (Caland and regional water data courtesy of Conly and Lee, 2010, unpublished data).

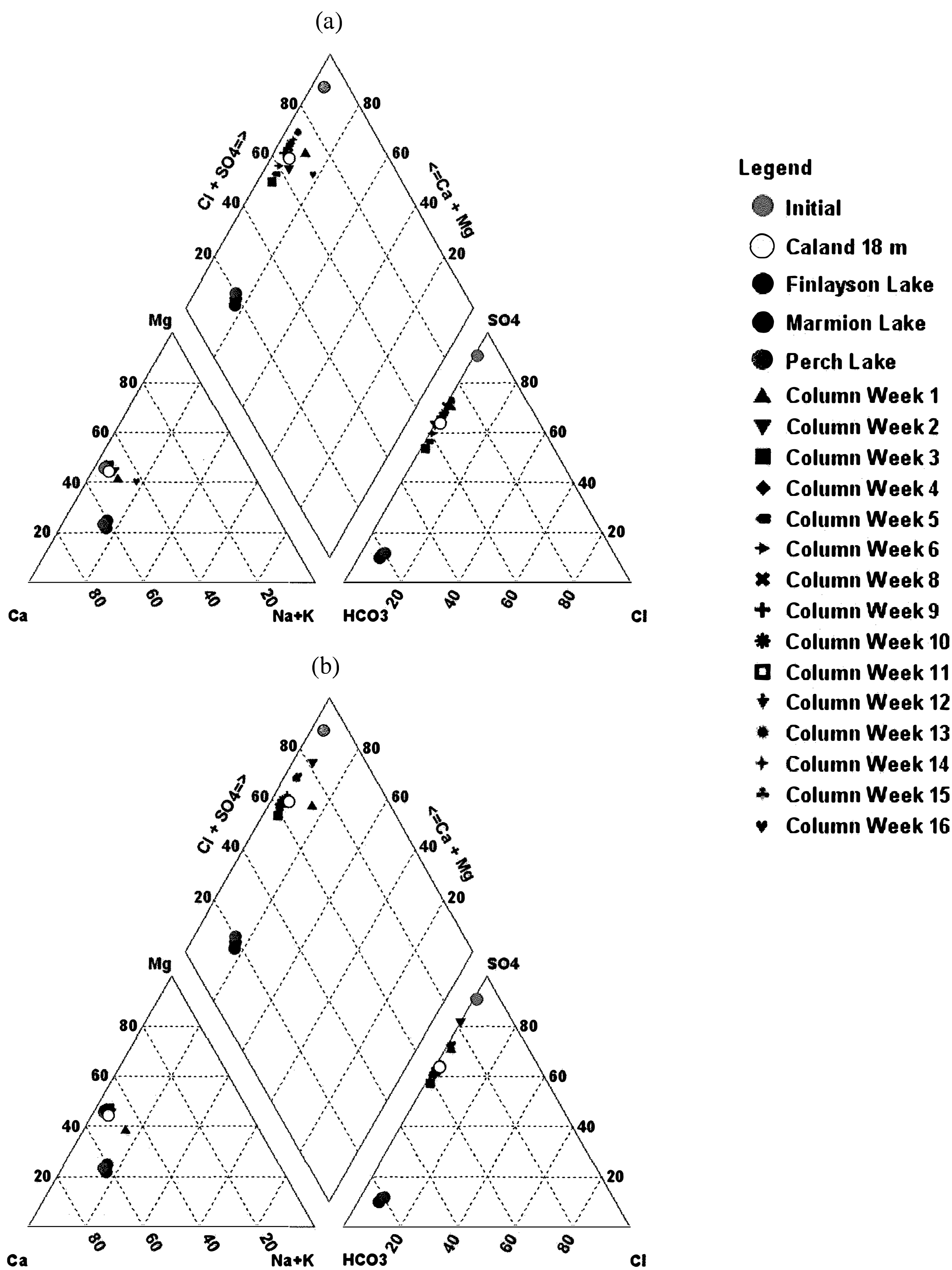


Figure 3.23: Piper diagrams for flow-through reactors (a) 3 and (b) 7. The composition of regional water bodies (Finlayson Lake, Marmion Lake and Perch Lake) and Caland Lake (18 m water) are plotted for comparison (Caland and regional water data courtesy of Conly and Lee, 2010, unpublished data).

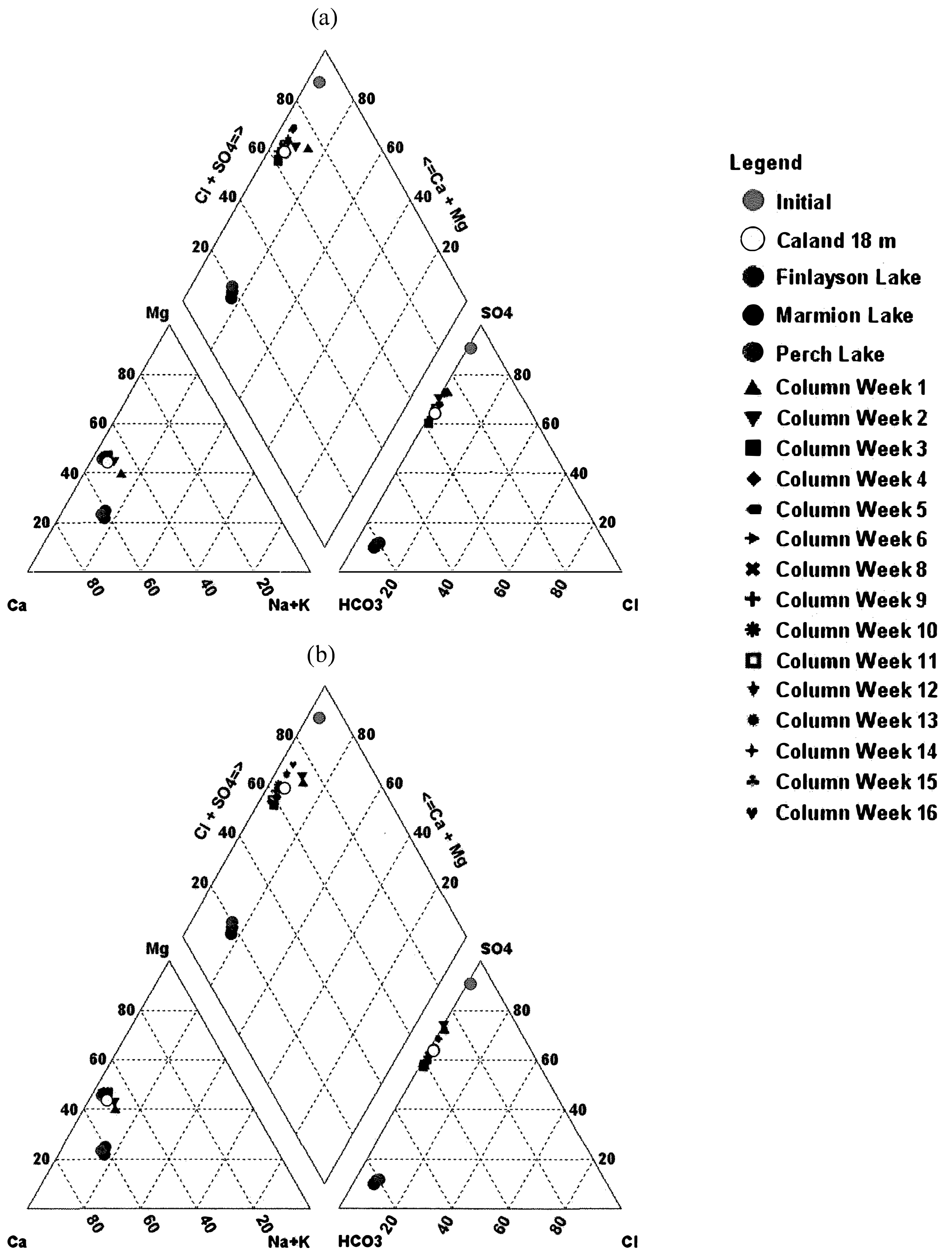


Figure 3.24: Piper diagrams for flow-through reactors (a) 4 and (b) 8. The composition of regional water bodies (Finlayson Lake, Marmion Lake and Perch Lake) and Caland Lake (18 m water) are plotted for comparison (Caland and regional water data courtesy of Conly and Lee, 2010, unpublished data).

3.3.6 Mineralogy of Flow-Through Reactor Media

The XRD pattern for the reactive medium from reactor 2 is shown in Figure 3.25 as a representation of the results from the XRD analyses. The XRD patterns for all other reactors are provided in Appendix 5. The results indicate that each of the reactors contained quartz, calcite and dolomite. As previously mentioned, α-Al_2O_3 was added to the powdered material prior to XRD analysis. The α-Al_2O_3 is best represented by a corundum peak. Calcite and dolomite are evident in the sample because of the Mosher carbonate rock that was added to the reactive media. Reactor 4 also contained clinoclore, reactor 5 contained rutile and reactor 8 contained albite.

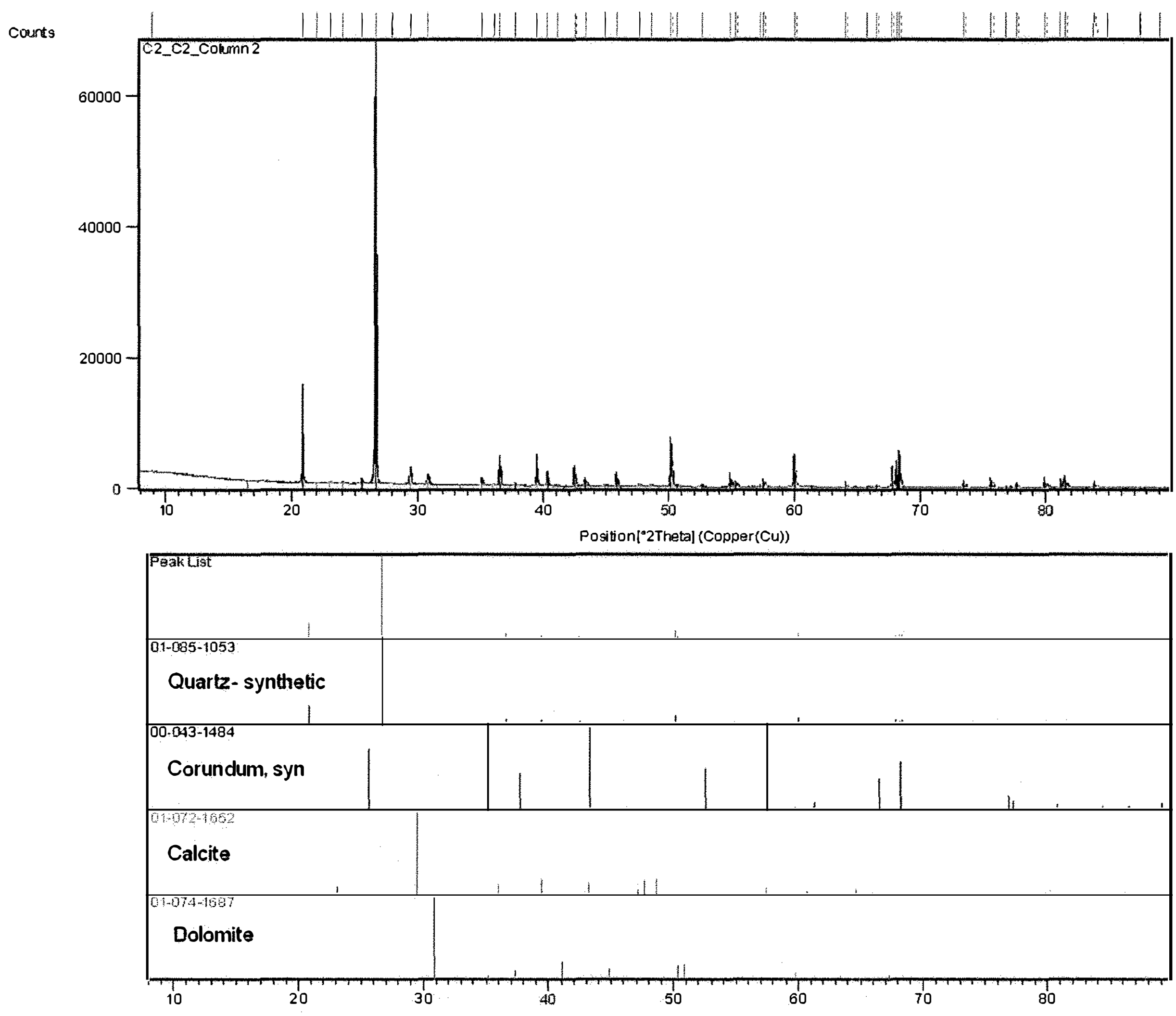


Figure 3.25: X-Ray diffraction patter of the post-experiment reactive mixture for flow-through reactor 2.

CHAPTER 4: DISCUSSION AND CONCLUSIONS

4.1 Batch Reactor Experiments

As sulphate is the primary concern with regards to toxicity (Goold, 2008), batch reactor experiments were conducted in order to determine the most suitable reactive mixture for sulphate reduction to use in the flow-through reactor experiments. Batch treatment 1, consisting of 15% organic matter, 15% creek sediment, 40% till and 30% carbonate rock, and treatment 2, consisting of 20% organic matter, 35% carbonate rock and 45% till, were successful in lowering the sulphate concentration in Hogarth pit lake water (Figs. 3.8a; 3.8b). Mixtures consisting of horse manure and wood chips were the most effective at reducing sulphate concentrations, with >99% of sulphate removed from the initial water. On the other hand, treatment 3, consisting of 15% organic matter, 15% molasses (to act as a nutrient for the SRB), 40% till and 30% carbonate rock, was not an effective medium for sulphate reduction, as the concentration of sulphate, major cations and trace metals all showed significant increases (Fig. 3.8c).

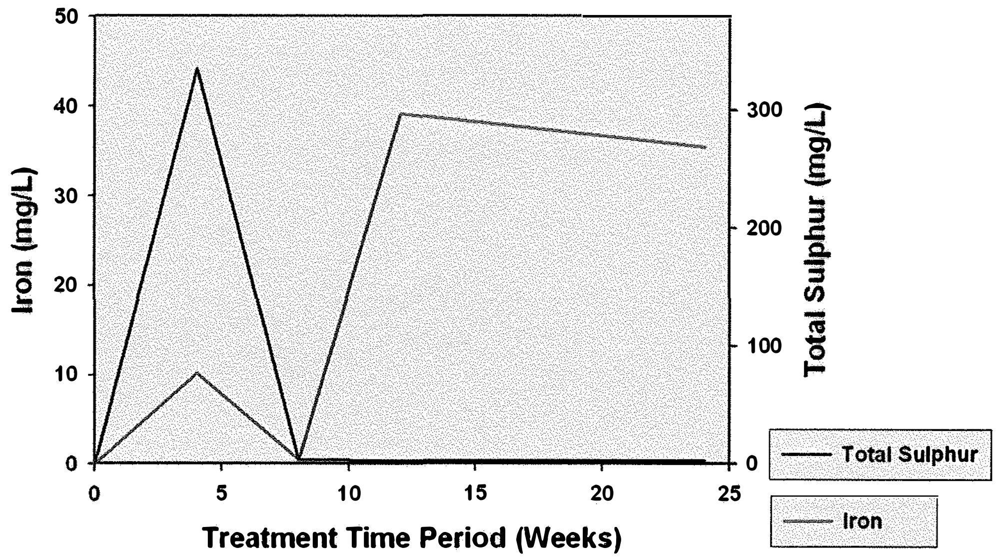
In order for sulphate reducing bacteria to thrive, they require a pH in the range of 5.0 to 8.0, and an anoxic and reduced environment with a redox potential lower than -100 mV, and nutrients (carbon, nitrogen and phosphorous; Waybrant et al., 2002; Walton-Day, 2003; Sasaki et al., 2008). Sulphidogenic activities, resulting in decreasing the sulphate content of batch reactor waters, were evident in treatments containing horse manure (treatments 1 and 2) and wood chips (treatment 1 only) by week 4 and in cow manure (treatment 1 only) by week 8 (Figs. 3.8a; 3.8b) Coinciding with the decrease in sulphate was an increase in pH ranging between 7.0 (treatment 2 wood chips) and 7.6 (treatment 1 horse manure); and decreased redox potential ranging between -140 (treatment 1 horse manure) and -227 (treatment 2 wood chips) mV, after sulphate acclimation. The increase in alkalinity (Figs. 3.7a; 3.7b) reflects bicarbonate production, and is additional evidence for bacterial sulphate reduction (e.g., Waybrant et al., 1998). However, no attempts were made to differentiate between bacterially produced bicarbonate and bicarbonate produced via interaction with carbonate.

The higher efficiency of substrates containing horse manure and wood chips to induce bacterial sulphate reduction is likely dependent on nutrient balance (carbon, nitrogen and phosphorous) of the organic component. Although the peat used in the experiments has a higher carbon and nitrogen content than horse manure and wood chips (Table 3.8) it was less effective at removing sulphate from Hogarth waters. On the other hand, phosphorus values were much higher in horse manure and cow manure than peat, but wood chips had a much lower phosphorus value than peat. Thus the phosphorus balance appears to have an effect on the bacterial sulphate reduction efficiency.

The results of treatment 3 for all organic substrates did meet the requirements favourable for sulphate reduction. Favourable conditions for redox values (generally less than -100 mV) were observed, but pH concentrations decreased to values between 5.0 and 6.0 and sulphate concentrations increased to greater than initial values. Although, the exact reason(s) why this treatment was not able to generate sulphate reduction is unclear, further investigation was deemed unnecessary as the other treatments generated sulphate reducing conditions.

The primary product of sulphate reduction is hydrogen sulphide. Sulphide concentrations were generally below detection for horse manure and wood chips in treatment 1. Sulphide concentrations were slightly higher for treatment 2, although concentrations never exceeded than 0.4 mg/L. The low concentrations may in part reflect analytical challenges in analyzing aqueous sulphide (Gilbert et al., 2004). However, it is feasible that aqueous sulphide was initially consumed in the precipitation of metal sulphides (e.g., Christensen et al., 1996; Benner et al., 1999). A comparison of iron and total sulphur concentrations of treatment 1 horse manure (Fig. 4.1a) and treatment 1 wood chips (Fig. 4.1b), shows that between weeks 4 and 8 in the horse

(a)



(b)

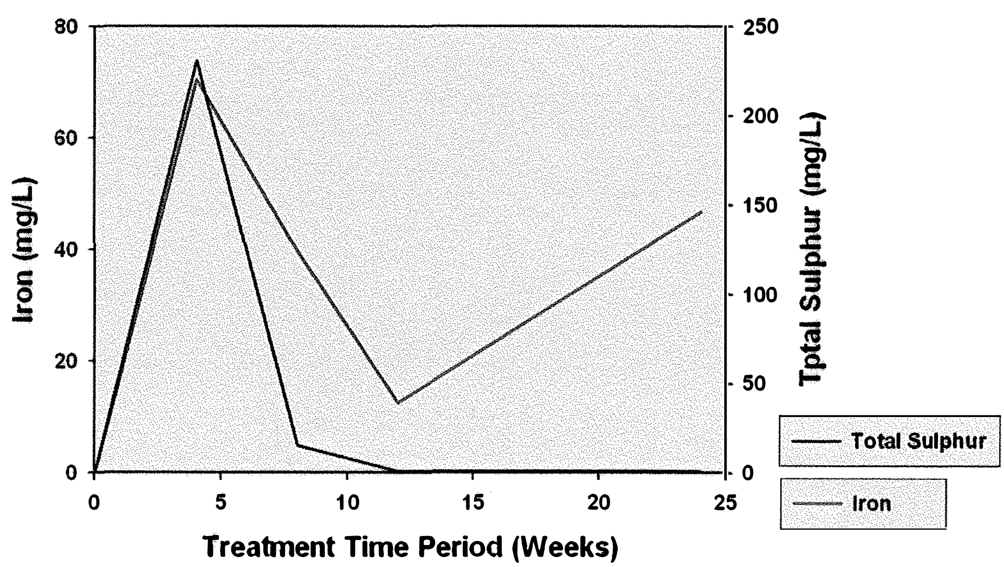


Figure 4.1: Iron versus sulphur for batch reactor experiments using treatment 1 with (a) horse manure and (b) wood chips.

manure, and weeks 4 and 12 in the wood chips, a mutual decrease in iron and total sulphur was occurring. This initial decrease is consistent with the removal of both iron and sulphur from the water due to the precipitation of iron sulphide. However, the precipitation of sulphide minerals was not confirmed by mineralogical analysis (XRD; Scanning Electron Microscopy - Energy Dispersive Spectroscopy (SEM-EDS)).

Concentrations for metals showed increasing trends for all reactive media in both treatments. Increases in metals are attributed to dissolution of metals within the reactive media (Table 3.7) specifically iron, which generally showed the highest increase. Creek sediment and glacial till contain significant quantities of acid-soluble iron (Table 3.4). In the batch reactor experiments, the bottles were sealed for the duration of the experiment and pH and redox conditions were favourable for sulphide precipitation. It is likely that the higher metal concentrations in the batch waters at the end of the experiment were due to leaching and desorption of metals from the reactive media. Consequently, metal toxicity is a possibility in a static system.

Treatment 1, which contained creek sediment, was chosen as the most suitable treatment for use in the flow-through experiments. Creek sediment may promote quicker acclimation of bacteria, as indicated by the earlier sulphate reduction in treatment 1. Inoculation of the reactors with SRB is not necessary to initiate sulphate reduction, but can shorten the lag phase significantly (Christensen et al., 1996). A mixture of horse manure and wood chips was chosen as the most viable nutrient for SRB in the flow-through experiments, as both were equally effective at promoting sulphate reduction and may increase the porosity of water flow through the reactor, more than a matrix composed solely of rock (Tsukamoto et al., 2004).

4.2 Flow-Through Reactor Experiments

4.2.1 Evidence for Sulphate Reduction

The most successful reactors for sulphate reduction were reactors 1 and 5 (two reaction chambers separated by silica sand), where the greatest degree of sulphate reduction (46% and 49%, respectively) was between weeks 3 and 4 (after SRB acclimation). In comparison, reactors 2 and 6 (two reaction chambers separated by carbonate rock) were the least successful at reducing sulphate. However, all reactors exhibited a significant decrease in sulphate concentrations (> 42%) in the first 8 weeks and remained below initial levels for the duration of the experiment. The extent of sulphate reduction is comparable to Waybrant et al. (2002) and Tsukamoto et al. (2004), who reported reduction rates of 42% and 45% in sulphate concentrations, respectively. In addition to the decrease in sulphate concentration, other evidence for sulphate reduction reactions that were evident after week 3 includes increases in alkalinity, bicarbonate, and pH, coupled with a decrease in redox potential.

The extent of sulphate reduction was not consistent within an individual reactor as illustrated by changes in sulphide, total sulphur, iron and redox for flow-through reactors 2 and 5 (Fig. 4.2). In the first 3 weeks of the experiments redox values drop significantly to -100mV, indicating anaerobic conditions and remained below this value in all reactors for the remainder of the experiment. This indicates that although aerated water was continually added to the system the reactors remained anaerobic. Sulphide concentrations of the treated waters were highly variable throughout the experiment; however, in all reactors, an initial increase in sulphide values was observed in the first 6-8 weeks. This is a further indicator that sulphidogenic activities are occurring in the first few weeks of the experiment. After the initial increase sulphide values are highly variable for the last 8-12 weeks of the experiment. One explanation for the observed variability may be reduction of sulphate to sulphide followed by oxidation of the sulphide to

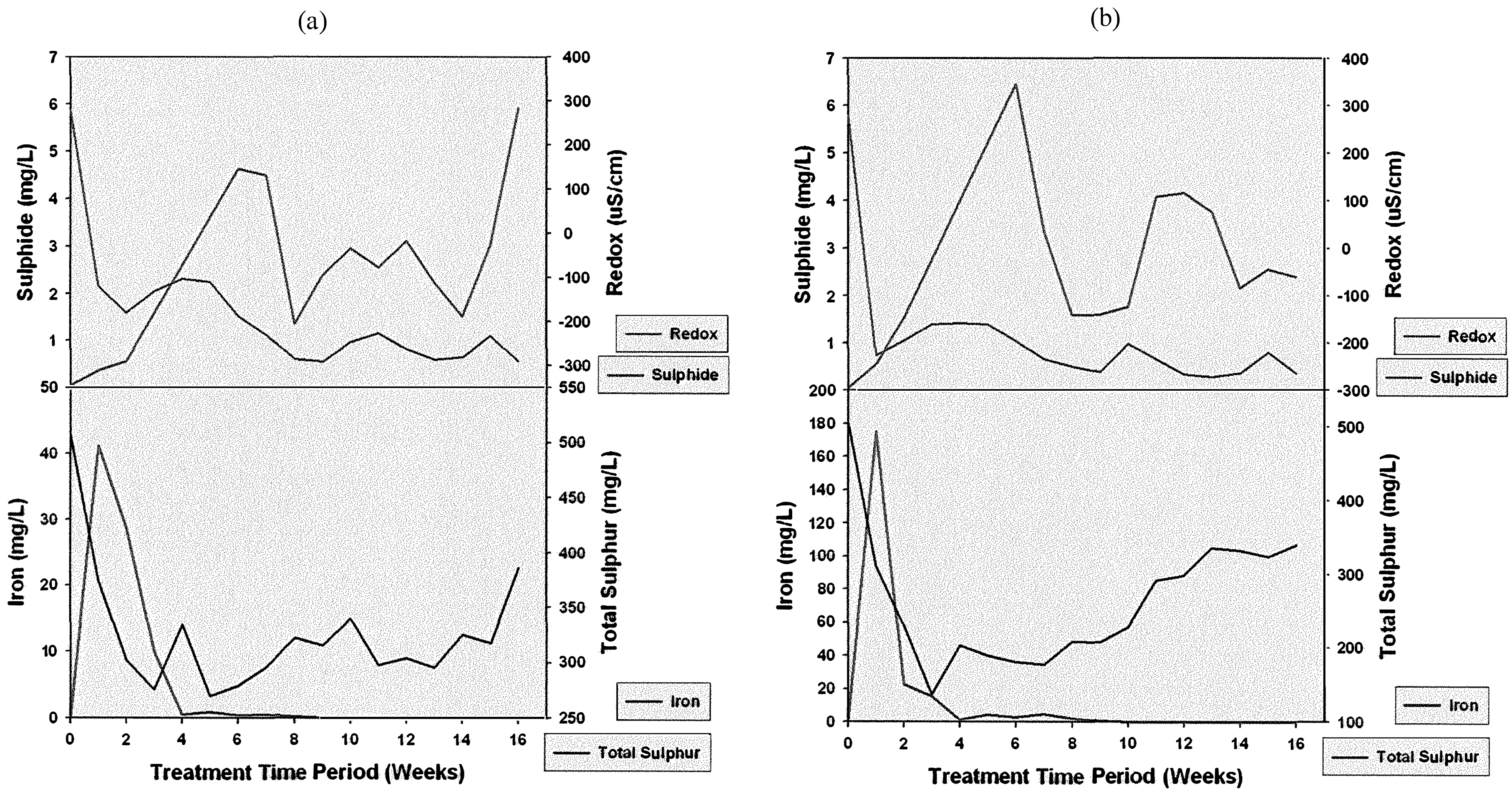


Figure 4.2: Variation in iron, sulphur, sulphide and Eh for flow-through reactors (a) 2 and (b) 5 from 0 to 16 weeks.

form sulphur species (Amos et al., 2004). However, this is inconsistent with anoxic conditions being preserved throughout the experiments. Alternatively, the variation in sulphide concentrations after 8 week may reflect a reduction in the extent of metal sulphide precipitation due to the limited availability of divalent metals (i.e., Fe) for sulphide formation. There is no direct mineralogical evidence (e.g., XRD; SEM-EDS) for the precipitation of metal sulphide minerals in any of the flow-through reactors. Precipitation of metal sulphides is inferred by the mutual decreases in iron and total sulphur (Figs. 4.2 and 4.3). After week 5, iron concentrations remain low (near initial concentrations) while sulphur concentrations underwent a progressive increase (although remained below initial concentrations). This may suggest that sulphide reduction was still occurring, albeit at lower efficiencies, without the precipitation of sulphide minerals. In addition, the maintaining of reducing conditions indicates that SRB activity is still occurring in the system, only at a slower rate than initially. This may be due to smaller population of SRB due to the consumption of nutrients by the bacteria in the system (e.g., Waybrant et al., 2002).

4.2.2 Factors Affecting the Efficiency of Sulphate Reduction

Apart from the need to maintain anoxic conditions and a source of sulphate reducing bacteria, the efficiency of sulphate reduction in the flow-through reactor experiments is influenced by:

- Availability of nutrients
- Availability of divalent metals
- Residence time and permeability of the reactor
- Internal structure of the reactor
- Anoxic oxidation of sulphide
- Exposure to oxidizing conditions

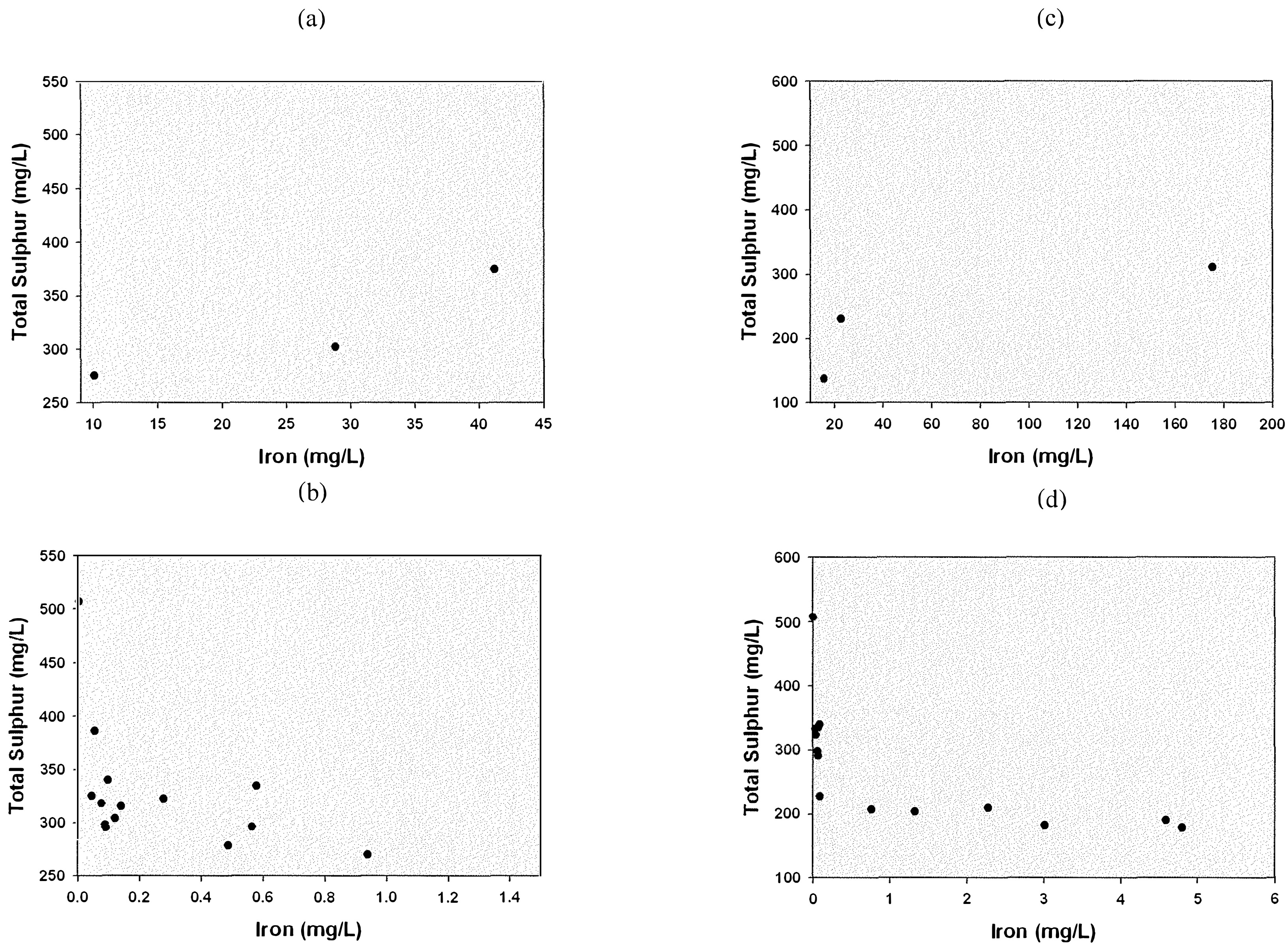


Figure 4.3: Iron versus total sulphur of waters from flow-through reactor 2 (a) weeks 1-3 and (b) weeks 4-16, and flow-through reactor 5 (c) weeks 1-3 and (d) weeks 4-16.

Availability of nutrients: As discussed earlier, sulphate-reducing bacteria require a carbon, nitrogen and phosphorous-based nutrient source in order to maintain biological activity. Batch reactor experiments demonstrated that organic components with higher phosphorous contents were more effective at inducing bacterial sulphate reduction. The importance of phosphorous was echoed in the flow-through reactor experiments. Phosphorus values in the initial reactive media (Table 3.5) were much higher than the concentration in the final reactor material (Table 3.6), indicating that phosphorous was consumed during sulphate reduction. However, nutrient supply does not appear to be the rate-limiting step for sulphate-reduction in the flow-through reactors, as anoxic conditions were maintained, sulphate-reduction continued (albeit at a reduced rate) and the availability of phosphorous (and assuming carbon and nitrogen based nutrients) were not fully exhausted.

Mixtures containing multiple sources of organic matter can be more effective than a single source on its own (i.e., sulphate reduction rates are higher in reactive mixtures containing multiple organic carbon sources; Waybrant et al., 1998; Neculita et al., 2007). Horse manure may not have the longevity to support a long-term system, but combining with other sources such as sawdust and other types of manure may promote the longevity of the system. Examples of other suitable inexpensive materials for PRB include municipal compost, sewage sludge, forestry waste and leaf mulch (Waybrant et al., 2002; Blowes et al., 2003). It may also be beneficial to combine organic sources with the SRB source (creek sediment) in an anaerobic environment to promote bacterial growth prior to the addition of mine water to the system (Neculita et al., 2007). This would help acclimate the bacteria and possibly eliminate the initial lag phase caused by SRB growth. The addition of a "nutrient" such as methanol or lactate to the stock water may also eliminate the lag time for SRB acclimation (Hammack and Edenborn, 1992). Studies have shown that the addition of sodium or potassium lactate to the system can help to promote sulphate reduction reactions by increasing the productivity of the bacteria (Gilbert et al., 2004; Dvorak et al., 1992).

Availability of divalent metals: For sulphate reduction to be effective, the aqueous sulphide product needs to complex with a divalent metal, resulting in removal of both sulphide and the metal from the water via precipitation of a metal sulphide phase. The initial Hogarth waters are metal-poor with Fe concentration of 0.005 mg/L and the combined concentration of all metals (including Fe) being 0.20 mg/L. Thus the availability of metals for sulphide precipitation is a potential problem in treating Steep Rock mine waters. The concentration of iron and other metals increased in the first week of the flow-through experiment (Figs. 3.15a and 4.4). This early increase in metal concentration of the treated waters is due to desorption of metals from organic constituents and limited dissolution of water or week-acid soluble phases in creek sediment, glacial till or carbonate sand. During weeks 2 and 3 the concentrations of iron and other metals were dramatically reduced in the treated waters for all reactors and remained near initial values for the remainder of the experiments. The decrease in metal concentrations was most pronounced in reactor 5 and less so in reactor 2 (Fig. 3.18a). Between weeks 1 and 3 of the experiment (Figs. 4.3a; 4.3c), as iron levels decreased, sulphur values also decreased due to bacterial sulphate reduction and removal of metals and sulphate possibly by precipitation of iron sulphides. After week 3 (Figs. 4.3b; 4.3d) the relationship changed and as sulphur levels increase and iron concentrations remained low, similar to initial Hogarth water. This reflects that sulphate was continually being added to the system and sulphate reduction was also continuing; however, the insufficient quantities of divalent metals available for sulphide precipitation may be partially responsible for the observed variation in the concentration of aqueous sulphide. Therefore, the availability of metals is perhaps the most critical rate-limiting step for treatment of Hogarth waters via bacterial sulphate reduction.

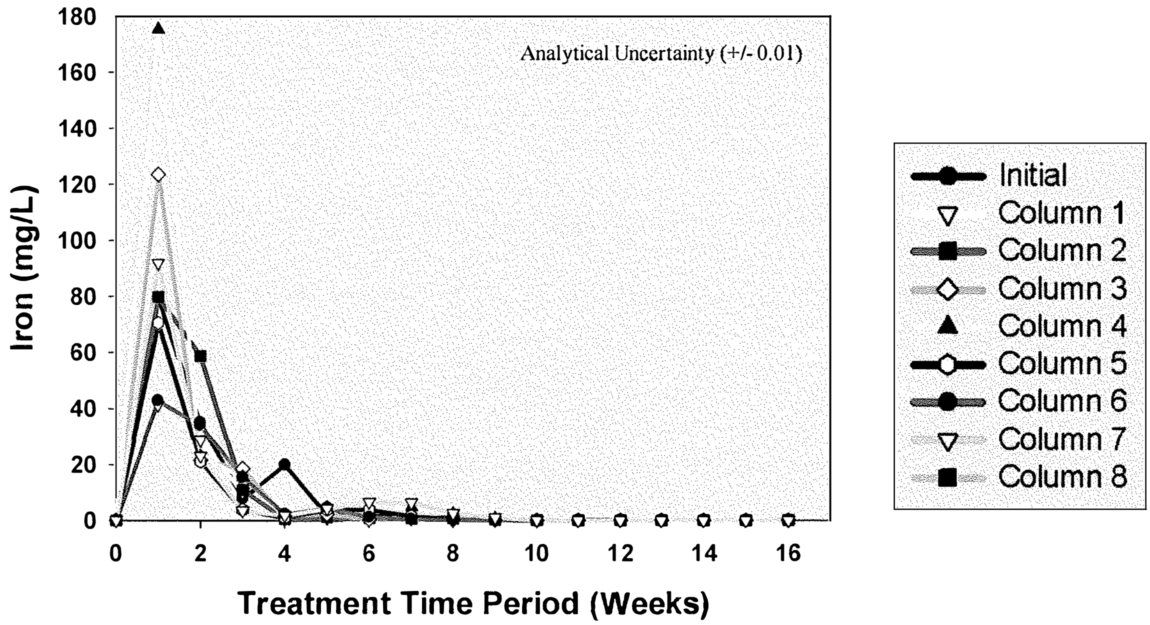


Figure 4.4: Variation in iron for all flow-through reactors (weeks 0-16).

Residence time and permeability of the reactor: It is important to consider residence time as a key factor in sulphate reduction, because it dictates the length of time that the water is allowed to react with the organic media (Benner et al., 1997; 2002; Herbert et al., 1998). As mentioned previously flow-through reactors 1-5, 2-6, 3-7 and 4-8 were run in duplicate. Although reactors 1 and 5 showed a similar success, reactor 1 had lower sulphate values (~200 mg/L) than reactor 5 (~ 600 mg/L) in the first 4 weeks of the experiment; however, after 5 weeks sulphate values increased throughout the rest of the experiment. Reactor 5 values remained lower, close to 600 mg/L for a longer period of time, until approximately week 8. It was noted that reactor 1 had a residence time of 71 hours and 40 mins, while reactor 5 had a residence time of 127 hours and 35 minutes. It is possible that the organic nutrients in reactor 5 were used at a slightly slower rate than in reactor 1, due to the increased residence time.

Dvorak et al. (1992) noted that an increase in residence time can increase sulphate reduction, but if the residence times are too long, the sulphide and alkalinity produced in the reaction may be unused.

It is possible that the differences in duplicate reactors are attributed to the residence time of the reactors. For example, reactors 1 and 5, which had notable differences in sulphate concentrations had the greatest difference in residence time, 71 hours and 127 hours, respectively. Reactors 4 and 8 also had a significant difference in residence time, 130 hours and 94 hours, respectively, but differences in sulphate concentrations were not significant. Whereas, reactors 2 and 6 showed several notable differences but had the smallest difference in residence time, 91hours and 92 hours, respectively. Also, residency time was only calculated at the beginning of the experiment. Several of the flow-through reactors were clogged by the end of the experiment (weeks 16 to 20), thus residence times progressively increased throughout the experiments.

Another possibility for the differences in duplicate reactors is the difference in the proportion of materials in the reactive media. As the reactive mixtures were homogenized prior to use, the variations in the proportions of components comprising the reactive mixture had on the effectiveness of sulphate reduction is considered negligible. However, the specific effects of even small mass variances on chemical heterogeneities were not assessed.

In field-scale bioreactor studies, it is generally accepted that the precipitation of metal sulphides occurs within a period of 3-5 days (Neculita et al., 1997). The longest residence time occurred in reactor 4 with a value of 130 hours and 20 minutes, which also had the lowest sulphate reduction (39.3 %) and might further suggest that the residence time was too long for proper sulphate reduction to occur. However, reactor 2 also had the lowest overall sulphate reduction (39.3%) but had the shortest residence time of 91 hours and 50 minutes, which may suggest that degradability of the organic matter, rather than residence time may be the limiting factor in the experiment; however, there is no evidence to support this theory.

As previously mentioned, short residence times may not allow adequate time for bacterial activity to precipitate metal sulphides and neutralize acidity. This could result in the reactor interior being acidified to the point that bacterial activity is inhibited (Dvorak et al., 1992). Accurate calculations on the hydraulic conductivity of the reactive medium would provide a better estimate on the residence time of the system. Benner et al. (2002) noted that even the slightest differences in hydraulic conductivity could have a significant affect on a PRB system. An increase in residence time can increase the reaction rate of sulphate reduction, but if the residence times are too long, the hydrogen sulphide and alkalinity that is produced in these reactions will go unused (Gilbert et al., 2004). Therefore, the hydraulic conductivity of a barrier is one of the most important factors when designing a PRB because of its affect on groundwater flow rates and retention times. In field-scale bioreactor studies, it has been noted that the precipitation of metal sulphides generally occurs within a 3-5 day period, and retention times that are shorter than 3 days may not allow the time necessary for SRB to precipitate metals (Neculita et al., 2007). However, if retention times are greater than 5 days, biomass may be flushed through the system and go unused (Neculita et al., 2007). The reactive mixture must be sufficiently permeable to ensure that the groundwater flows through the wall in order for treatment of the groundwater to occur. However, the barrier should not be too permeable so that groundwater rushes through the system and result in insufficient residence times to allow sulphate reduction to occur (Waybrant et al., 1998). A flow-through reactor study which increases the flow path length would create a longer residence time as well as add additional organic matter to the system and theoretically decrease the degradability. Accurate measurements on hydraulic conductivities of both the surrounding aquifer and the reactive media would be necessary before the implementation of test cells at the site.

Internal Structure of the Reactor: The internal structure of the flow-through reactors are shown of Figure 2.3. Duplicate reactors 2 and 6, which contained two reaction chambers separated by carbonate rock, generally had similar sulphate values, although during weeks 9 and 10, the sulphate concentration in reactor 6 decreased, but reactor 2 remained similar. Also, there was a significant increase of chloride values in reactor 6 only at week 13 and a slight increase in alkalinity at week 15 in reactor 2 only. Reactors 3 and 7 had three reaction chambers separated by silica sand. The only notable difference between these reactors was a decrease in sulphate in reactor 7 only at week 7, while reactor 3 increased, and higher sulphate values were also occurring in only reactor 3 between weeks 8 and 10. Reactors 4 and 8 both had a single reaction chamber and there were no notable differences between the two.

The reactor chambers seem to have an effect on effective sulphate reduction, since comparisons between duplicate reactors showed varying success; however, it is unclear how this may occur. One reason may be that it is due to settling of the reactive media within the reactor, as water was introduced. Clogging issues were noted at week 20 in duplicate reactors 2 and 6, which showed varying sulphate reduction, and may be caused by the larger grain size of the carbonate rock used as a separating layer between the chambers.

The differences between the structures of the reactors are due to differences in composition of the reactive media within. Great care was taken when weighing and adding the volume of material but, as mentioned, slight differences in composition may cause significant changes in reactor efficiency.

Anoxic oxidation of sulphide: The gradual increase in sulphate concentration in all flow-through reactors (after weeks 4-8) and the variable nature of sulphide concentration may in part reflect anoxic oxidation of sulphide. Sulphide oxidation under anoxic conditions will occur as a result of denitrification of the organic media (Krishnakumar and Manilal, 1999; Mahmood, et al., 2007), where:

$$3HS^- + 8NO_2^- + 5H^+ \rightarrow 3SO_4^- + 4N_2 + 4H_2O$$

Thus sulphide produced by bacterial sulphate reduction may have been oxidized by nitrate produced in the reactor and converted to sulphate. Speciation calculations using PRHEEQC were performed to determine the speciation of aqueous sulphide in water from flow-through reactor 1 at week 16. These calculations showed that >90% of the aqueous sulphide in the system was HS^- and coupled with the low redox potential, there is reasonable evidence in support for anoxic oxidation of sulphide. However, nitrate concentrations were not measured thus it is not possible to fully evaluate the role of anoxic sulphate reduction. Regardless of the potential for anoxic sulphide oxidation, the role it has in generating the observed increase in sulphate is subordinate to availability of metals and nutrients the their effect on the efficiency of sulphate reduction.

Exposure to oxidizing conditions: Exposure to oxygen can inhibit the effectiveness of SRB (Neculita et al., 2007) and a PRB design should include a protective cap (about 30 cm thick) that would be placed over the barrier to help keep the system anaerobic and minimize O_2 diffusion into the barrier (Benner et al., 1999). Cover materials have also been used to limit the amount of water infiltration into the barrier, which may increase significantly during spring flooding, and would help to minimize erosion of the reactive mixture or other waste materials on-site (Blowes et al., 2003).

The design of the flow-through system prevented the exposure of reactive mixture and treated waters to oxygen. Thus oxygenation of the reactor was not a factor in these experiments. The redox values, ranging from approximately -100 to -300 mV, for all flow-through reactors indicates that anoxic conditions were maintained and that precautions such as parafilm sealing all valve fittings and use of Ar gas on the outflow side of the flow-through system limited the diffusion of oxygen into this system. With respect to oxygen incursion, it is most critical on the outflow side of the system, as the inflowing water for treatment is oxygenated.

Summary: Of the factors affecting the efficiency of sulphate reduction, the availability of metals and nutrients are the most critical. However, these two factors alone are not entirely responsible for the observed progressive increases in sulphate concentrations in flow-through waters following the peak period of sulphate reduction. Processes like anoxic oxidation of sulphide likely occurred; however, quantifying its role is not possible with the data available. Regardless, its role is likely minor and has a greater influence on the concentration of sulphide than sulphate in the treated waters. Rather the progressive increase in sulphate reflects:

1. Decrease in the rate of sulphate reduction due to limited availability of divalent metals and nutrients, thus waters entering the reactors are not fully treated; and,
2. Subsequent mixing and dilution of sulphidic waters with "untreated" Hogarth water.

The nature of mixing and dilution is difficult to quantitatively assess. However, residence time and the internal structure of the reactor are the most critical factors. The increased residence time of the flow-through experiments may have resulted in the sulphidic waters that formed early in the experiments having not been evacuated from the reactors. However, with time the role of mixing and dilution diminishes as less sulphide is being produced, and the higher sulphate concentrations are largely reflecting the passage of untreated waters.

4.2.3 Comparison to Regional Water and Caland Pit Lake Water

Sulphate concentrations from weeks 3 to 5 (<300 mg/L) of flow-through reactor 1 water is comparable to Caland pit lake water, which has an average sulphate concentration of between 227 and 379 mg/L (Table 4.1); however, flow-through reactor waters were characterized by higher conductivity and elevated concentrations of calcium, magnesium, sodium and iron. The similarity in sulphate concentrations indicates that PRB treated waters would not be acutely or chronically toxic due to sulphate, as Caland waters are non-toxic and the pit lake hosted a fish farm from 1989 to 2009.

Although sulphate was effectively reduced in Hogarth pit lake water using a bench-scale PRB, the lowest concentrations of sulphate achieved are still significantly higher than values of regional lakes. Marmion Lake (northeast and up gradient of the site), Finlayson Lake (north and up gradient of the site), and Perch Lake (west and down gradient of the site) each have sulphate concentrations that are <5 mg/L (Conly and Lee, 2010, unpublished data). Values for conductivity, pH, alkalinity, barium, calcium, potassium, magnesium, manganese, sodium, sulphur and zinc were also higher in the flow-through reactor waters than in the regional lakes (Conly and Lee 2010, unpublished data). The concentrations of all other metals in the flow-through reactor waters are similar to regional lake waters. While the potential outflow waters from a PRB that is treating Hogarth pit lake water may not be sulphate toxic, the Caland-like concentrations are still likely undesirable for discharge into the West Arm.

Table 4.1. Average water composition of Caland pit lake for 2005-2008 (data from Goold, 2008, Godwin, 2010; Conly and Lee, 2010, unpublished data).

Description	2 m	18 m	40 m	x-1 m
pH	8.1	7.8	7.5	7.4
Conductivity	681	692	867	1010
TDS	475	481	656	734
Alkalinity	130	133	162	173
Cl^-	4.44	4.57	7.75	9.58
SO_4^{2-}	228	236	314	379
S^{Total}	73.5	74.4	98.9	107.8
Ca	75.9	77.1	100.3	114.1
Mg	38.2	41.4	48.4	56.7
Na	8.46	8.66	12.84	15.08
K	3.48	3.50	4.20	4.48
Total Metals	0.16	0.10	0.18	1.18

Total metals include aluminum, barium, copper, iron, manganese, nickel and lead.

Consequently, further treatment would be required. Fortunately, it may be feasible to link a PRB to another passive treatment system, such as a constructed wetland that is downgradient of a PRB. Wetlands are a natural passive treatment system for AMD and a constructed wetland could theoretically be left to itself once established. Wetlands can remove sulphate and heavy metals by using sulphate reduction reactions from SRB, similar to the process used by PRBs (Webb et al., 1998). The key factors to consider in the construction of an engineered wetland are flow rate, drainage through the substrate, and choice of SRB and plant species. The choice of plant species is important because it must be locally available and also have the potential to promote sulphate reduction. Vancook (2005) determined that wetland plants, native to the region, could be used to reduce sulphate concentrations of Caland pit lake water. Due to similarities between Caland water and flow-through reactor waters (Figs. 3.21, 3.22, 3.23 and 3.24), it is feasible to suggest that further reduction of sulphate concentrations of Hogarth pit lake water could be accomplished using a wetland ecosystem. The ideal system would entail a PRB, consisting of two reaction chambers with horse manure and wood chips as the organic sources and would treat the water before entering a constructed wetland.

4.3 Future Work

Although efforts were taken to determine the mineralogy of the flow-through reactive media, a more detailed description of the mineralogy would be helpful in determining the chemical reactions occurring in the system. It is possible that sulphide precipitates occur at concentrations below the detection of the XRD (~2-5 modal%). SEM-EDS and sequential bulk-rock extractions could be used to identify precipitated phases. Also SEM image analysis would provide important information to better constrain the nature of water-mineral/organic reactions within the flow-through reactors.

The batch and flow-through experiments were run at room temperature (~20°C). However, Dvorak et al. (1992) noted that raising the temperature range of the experiment to 25° – 35°C) to stimulate bacterial activity may increase sulphate reduction rates. Conversely, a potential drawback to sulphate reduction-based treatment systems is that their efficiency is reduced by cold temperatures (Tsukamoto et al., 2004). Thus it would be worthwhile to assess the effect of seasonal temperature variations on the efficiency of sulphate reduction. In particular it would be important to determine if a system could be designed for installation at greater burial depths (e.g., below the frost line). The advantage of such a system is that temperatures would be more constant and would allow for water flow and sulphate reduction in the winter months. Although biological activity would be reduced, in comparison to the summer activity of a shallow PRB, the ability to have sulphate reduction occurring year round may result in higher overall efficiencies.

Another factor affecting rate and extent of sulphate reduction is the availability of nutrients for SRB growth. If the nutrient supply was exhausted, rates of sulphate reduction may have decreased or stopped altogether. A better understanding of the role of the primary nutrients, carbon, nitrogen and phosphorus, is required. In particular, it is necessary to determine what nutrient levels are required, in particular phosphorous, as it appears to be the most critical nutrient, to maintain sulphate reduction over a longer period of time.

A critical problem encountered with the flow-through reactors was a progressive reduction in permeability, in particular between weeks 16 and 20, because of clogging due to sulphide precipitation (?) and compaction. Any field-based system would have to ensure greater longevity, while maintaining efficiencies in sulphate reduction. Improved efficiencies for sulphate reduction occur with greater surface area of the reactive media. On a volume to surface area basis, a finer-grained reactive medium would in theory be more effective; however, it would be subject to a more rapid reduction in permeability due to clogging by mineral precipitates. A reactive medium with large pore spaces, low surface area, and a large void volume is generally preferred in a full-scale barrier design because it minimizes plugging of the system (Tsukamoto et al., 2004). However, it is important for future investigations to assess the critical balance between surface area and pore space of a field bioreactor.

4.4 Conclusions

Bacterial sulphate reduction is a low-cost, low-maintenance technique capable of treating mine waters with increased sulphate content. Low cost can be achieved especially if locally sourced materials could be used. The results demonstrate the potential of SRB for reducing sulphate concentrations at the Steep Rock site but also highlight the importance of considering biodegradability of the organic substrate and residence time in the overall performance of the system. Batch reactor experiment data showed a high success for decreasing sulphate levels. Horse manure and wood chips (> 99% sulphate reduction) with the addition of creek sediment, carbonate rock, and till, were chosen as the reactive media to be used in the reactor experiments. Sulphate reduction was evident after 4 weeks, with increases in pH, alkalinity and bicarbonate, and decreases in redox potential to < -100 mV. Although sulphate values gradually increased after week 6 of the experiment, sulphate reduction was still evident due to low redox values, continued bicarbonate production and the fact that sulphate values did not increase, even though stock water was continually introduced to the system.

The most successful flow-through reactors in terms of lowering sulphate values were the reactors with two reaction chambers separated by silica sand. The reactive chambers contained 7.5% horse manure, 7.5% wood chips, 15% creek sediment, 30% carbonate rock and 40% glacial till. The treatments in reactors 1 and 5 showed a sulphate reduction of 46% and 49%, respectively. Once SRB were acclimated after 3 weeks, sulphate reduction rates were similar to other research with at least an average 39% reduction in all reactors. Flow-through reactor 1 showed an initial sulphate reduction to <300 mg/L between weeks 3 and 5, which has a similar value to the water found in Caland pit. A previous study at the site concluded that Caland water could be treated by a wetland ecosystem. It is reasonable to conclude that a treatment system that consisted of a PRB flowing into a constructed wetland has the potential to reduce the increased sulphate levels encountered at Hogarth Pit Lake.

The degradability of organic nutrients and the residence time are the limiting factors in the life span of a PRB. Therefore, the longevity of organic nutrients should be considered in any future research. Also, a study to determine the hydraulic conductivities and residence times of both the reactive media within a PRB, as well as within local aquifer material at the chosen location, would be beneficial to subsequent research. Future research could also consider reactor experiments that analyze multiple sources of organic material within a reactive media or could consider running the reactors over a longer flow path.

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APPENDICES

APPENDIX 1

H_2S REAGENTS AND STANDARDS

Amine-Sulphuric acid stock

Dissolve 2.7g N,N-dimethyl-p-phenylene diamine oxalate in a cold mixture of 50 mL H_2SO_4 and 20 mL DDW. Cool and Dilute to 100 mL with DDW. Store in a dark glass bottle.

Amine- H_2SO_4 reagent

Dissolve 2.5 mL of Amine-sulphuric acid stock solution with 1+1 H_2SO_4 in a 50 mL volumetric flask and bring to the mark. This solution must be clear. Store in a dark glass bottle. Prepare fresh daily.

Ferric Chloride solution

Dissolve 10 g $FeCl_3{\bullet}6H_2O$ in 4 mL of DDW. Makes approximately 10 mL. Store in a 25 mL dispensing bottle.

1+1 H_2SO_4

Carefully mix 50 mL concentrated H_2SO_4 to 50 mL DDW, allow to cool. Store in a glass bottle.

Diammonium hydrogen phosphate solution

Dissolve 10 g $(NH_4)_2HPO_4$ in 20 mL DDW. Store in a glass bottle. Make the amount required for the number of samples only (3 mL per sample).

Sulphide Stock Solution

Weigh 0.5 g $Na_2S{\bullet}9H_2O$. Rinse the crystals 2 times with 50 mL of DDW. Dissolve the remaining solid in 200 mL DDW using a 500 mL volumetric flask. Add 0.5 mL of 0.01 N NaOH, and bring to volume with DDW. Store in a dark glass bottle. Confirm the concentration by titration with sodium thiosulphate and standardize prior to analysis.

Intermediate stock sulphide standards

Prepare daily from the Sulphide Stock Solution. Dilute 1.0 mL of Stock in 25 mL of DDW.

APPENDIX 2

WATER CHEMISTRY MINIMUM DETECTABLE LIMITS AND STANDARD DEVIATION

WATER CHEMISTRY MINIMUM DETECTABLE LIMITS (MDL) AND STANDARD DEVIATION

Parameter	MDL	Units	Standard Deviation	
			Batch	Flow
pH*	0-14	n/a	0.5	0.5
Conductivity*	10 μS to 200 mS	μS/cm	158	158
TDS*	0 to 4000	mg/L	-	-
Redox Potential*	-2000 to +2000	mV	35	35
Alkalinity	1.0	mg $CaCO_3$/L	27.2	7.8
Bicarbonate	1.0	mg/L	27.0	6.1
Chloride (Cl^-)	0.05	mg/L	2.1	2.1
Sulphate (SO_4^{2-})	0.05	mg/L	51.3	72.7
Sulphide (S^{2-})	0.01	mg/L	0.01	0.01
Total Calcium	0.005	mg/L	16.8	11.1
Total Magnesium	0.01	mg/L	18.3	6.1
Total Sodium	0.01	mg/L	2.1	3.2
Total Potassium	0.01	mg/L	5.2	0.4
Total Aluminum	0.015	mg/L	0.01	0.02
Total Arsenic	0.025	mg/L	0.01	0.01
Total Barium	0.025	mg/L	0.01	0.01
Total Cadmium	0.001	mg/L	0.01	0.01
Total Chromium	0.005	mg/L	0.01	0.01
Total Cobalt	0.01	mg/L	0.01	0.01
Total Copper	0.005	mg/L	0.01	0.01
Total Iron	0.005	mg/L	0.3	0.01
Total Lead	0.015	mg/L	0.01	0.01
Total Manganese	0.001	mg/L	0.03	0.03
Total Nickel	0.005	mg/L	0.01	0.01
Total Sulphur	0.05	mg/L	30.7	18.7
Total Vanadium	0.01	mg/L	0.01	0.01
Total Zinc	0.005	mg/L	0.01	0.01

*- range reported; not MDL.

APPENDIX 3

BATCH REACTOR EXPERIMENT DATA

Conductivity (uS/cm)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	2329	1413	5070	6438	6639
Duplicate	2329	940		4858	4290
Straw	2329	1315	5739	4971	4910
Duplicate	2329		4041		4160
Peat	2329	708	2290	2083	2055
Duplicate	2329			2033	
Horse Manure	2329	743	3656	2165	2626
Duplicate	2329	616	3400		
Wood Chip	2329	641	1921	1438	1503
Duplicate	2329			1332	
Treatment 2					
Cow Manure	2329	1722	8384	6907	6828
Duplicate	2329	1437		6402	6388
Straw	2329	1479	4514	4219	4192
Duplicate	2329		2694		4402
Peat	2329	646	2231	2035	1930
Duplicate	2329			2047	
Horse Manure	2329	753	3125	3132	2468
Duplicate	2329	1066	4634		
Wood Chip	2329	814	2149	1819	1271
Duplicate	2329			1849	
Treatment 2					
Cow Manure	2329	4227	18260	9278	21410
Duplicate	2329	4050		1066	15930
Straw	2329	4186	15520	1411	15040
Duplicate	2329		15220		14340
Peat	2329	4102	17160	15190	16340
Duplicate	2329			14780	
Horse Manure	2329	4166	17050	15020	15260
Duplicate	2329	3764	15140		
Wood Chip	2329	617	16530	13570	15050
Duplicate	2329			13630	
Water Only	2329	604	2042	1972	2050
Duplicate	2329	656	2048		1999

Cells with no values indicate that a duplicate was not taken.

Aluminum (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	<0.005	1.595	6.358	0.976	0.362
Duplicate	<0.005	0.170		0.517	0.892
Straw	<0.005	0.604	5.958	1.170	0.815
Duplicate	<0.005		1.156		0.296
Peat	<0.005	0.063	0.126	1.461	0.617
Duplicate	<0.005			0.108	
Horse Manure	<0.005	0.088	0.369	1.221	0.671
Duplicate	<0.005	0.031	0.345		
Wood Chips	<0.005	0.058	0.118	0.056	0.081
Duplicate	<0.005			0.371	
Treatment 2					
Horse Manure	<0.005	0.059	0.142	0.924	0.489
Duplicate	<0.005	0.384	1.112		
Cow Manure	<0.005	0.374	3.255	0.670	0.410
Duplicate	<0.005	1.217		0.978	0.480
Straw	<0.005	0.382	9.223	0.769	0.509
Duplicate	<0.005		0.174		0.788
Wood Chips	<0.005	0.461	0.110	0.285	0.118
Duplicate	<0.005			0.339	
Peat	<0.005	0.449	0.237	0.134	2.387
Duplicate	<0.005			0.273	
Treatment 2					
Horse Manure	<0.005	56.0	11.8	7.90	7.74
Duplicate	<0.005	42.200	10.533		
Cow Manure	<0.005	69.2	19.2	8.10	5.89
Duplicate	<0.005	58.8		5.42	4.34
Straw	<0.005	72.9	32.4	16.5	10.2
Duplicate	<0.005		9.89		5.30
Peat	<0.005	63.0	12.4	8.68	10.0
Duplicate	<0.005			12.402	
Wood Chips	<0.005	73.4	36.3	57.8	30.2
Duplicate	<0.005			48.0	
Water Only	<0.005	0.024	0.016	0.012	0.022
Duplicate	<0.005	0.054	0.010		0.013

Arsenic (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	<0.025	<0.025	0.041	<0.025	<0.025
Duplicate	<0.025	<0.025		<0.025	0.028
Straw	<0.025	<0.025	0.025	<0.025	<0.025
Duplicate	<0.025		0.028		0.023
Peat	<0.025	<0.025	<0.025	<0.025	<0.025
Duplicate	<0.025			<0.025	
Horse Manure	<0.025	<0.025	0.048	<0.025	0.035
Duplicate	<0.025	<0.025	<0.025		
Wood Chips	<0.025	<0.025	<0.025	<0.025	<0.025
Duplicate	<0.025			<0.025	
Treatment 2					
Cow Manure	<0.025	<0.025	<0.025	<0.025	<0.025
Duplicate	<0.025	<0.025		<0.025	<0.025
Straw	<0.025	<0.025	0.028	<0.025	<0.025
Duplicate	<0.025		<0.025		<0.025
Peat	<0.025	<0.025	<0.025	<0.025	<0.025
Duplicate	<0.025			<0.025	
Horse Manure	<0.025	<0.025	<0.025	0.029	0.036
Duplicate	<0.025	<0.025	<0.025		
Wood Chips	<0.025	0.033	<0.025	<0.025	<0.025
Duplicate	<0.025			<0.025	
Treatment 3					
Cow Manure	<0.025	0.246	0.189	0.045	0.127
Duplicate	<0.025	0.239		0.052	0.101
Straw	<0.025	0.284	0.275	0.115	0.170
Duplicate	<0.025		0.158		0.100
Peat	<0.025	0.246	0.135	0.039	0.094
Duplicate	<0.025			0.082	
Horse Manure	<0.025	0.239	0.130	0.051	0.108
Duplicate	<0.025	0.066	0.128		
Wood Chips	<0.025	0.237	0.112	0.077	0.126
Duplicate	<0.025			0.105	
Water Only	<0.025	<0.025	<0.025	<0.025	<0.025
Duplicate	<0.025	<0.025	<0.025		<0.025

Cells with no values indicate that a duplicate was not taken.

Sulphate (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	1423.36	1294.19	982.10	96.44	4.09
Duplicate	1423.36	1110.82		8.05	894.70
Straw	1423.36	1375.87	1433.83	1200.37	4.51
Duplicate	1423.36		2155.86		499.40
Peat	1423.36	1368.44	1958.85	1180.17	1165.00
Duplicate	1423.36			1261.28	
Horse Manure	1423.36	958.60	4.95	1.47	3.95
Duplicate	1423.36	992.07	8.80		
Wood Chips	1423.36	726.80	72.86	9.36	2.12
Duplicate	1423.36			44.83	
Treatment 2					
Cow Manure	1423.36	1205.90	1992.43	546.45	374.40
Duplicate	1423.36	1231.01		459.00	122.40
Straw	1423.36	1405.51	2171.67	1131.21	297.70
Duplicate	1423.36		5.84		470.50
Peat	1423.36	1384.08	2121.05	1252.73	1321.30
Duplicate	1423.36			1209.72	
Horse Manure	1423.36	804.19	2.08	49.76	6.10
Duplicate	1423.36	1036.30	1518.44		
Wood Chips	1423.36	1404.48	1391.24	673.65	27.90
Duplicate	1423.36			481.04	
Treatment 3					
Cow Manure	1423.36	1866.71	3431.60	716.92	2193.70
Duplicate	1423.36	1759.58		862.43	2199.60
Straw	1423.36	2011.26	3284.93	1978.62	2204.20
Duplicate	1423.36		3555.70		2284.70
Peat	1423.36	1989.92	164.99	1848.55	2095.10
Duplicate	1423.36			1851.63	
Horse Manure	1423.36	1516.74	3214.11	1924.78	2111.70
Duplicate	1423.36	1692.84	3137.66		
Wood Chips	1423.36	2006.42	1657.35	1911.35	1973.10
Duplicate	1423.36			1924.92	
Water Only	1423.36	1446.86	2264.34	1432.79	1535.10
Duplicate	1423.36	1459.08	2410.59		1519.40

Calcium (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	316.3	292.2	243.8	160.6	126.4
Duplicate	316.3	322.3		90.3	330.0
Straw	316.3	555.5	236.5	294.8	116.8
Duplicate	316.3		310.5		327.4
Peat	316.3	540.0	388.7	409.4	420.5
Duplicate	316.3			402.7	
Horse Manure	316.3	346.7	225.2	180.3	140.5
Duplicate	316.3	337.5	220.4		
Wood Chips	316.3	383.7	221.0	155.8	113.7
Duplicate	316.3			146.9	
Treatment 2					
Cow Manure	316.3	419.9	188.2	138.8	146.8
Duplicate	316.3	298.0		160.0	152.9
Straw	316.3	588.0	454.9	325.3	293.5
Duplicate	316.3		202.5		303.7
Peat	316.3	550.7	430.1	412.0	448.0
Duplicate	316.3			373.1	
Horse Manure	316.3	367.0	200.6	158.7	113.5
Duplicate	316.3	309.0	342.8		
Wood Chips	316.3	531.0	266.7	234.1	117.6
Duplicate	316.3			243.9	
Treatment 3					
Cow Manure	316.3	4104	2371	1570	2955
Duplicate	316.3	3661		1905	3538
Straw	316.3	4157	2298	2052	2656
Duplicate	316.3		2235		2561
Peat	316.3	4620	3432	3012	4914
Duplicate	316.3			3540	
Horse Manure	316.3	4641	2951	2778	4074
Duplicate	316.3	2832	2699		
Wood Chips	316.3	4715	3108	2666	4187
Duplicate	316.3			3003	
Water Only	316.3	330.5	291.7	291.9	301.8
Duplicate	316.3	309.9	285.8		307.4

Cells with no values indicate that a duplicate was not taken.

Cadmium (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	<0.001	0.001	0.001	<0.001	0.002
Duplicate	<0.001	0.003		<0.001	0.002
Straw	<0.001	<0.001	0.001	<0.001	0.003
Duplicate	<0.001		0.001		0.002
Peat	<0.001	<0.001	<0.001	<0.001	0.001
Duplicate	<0.001			<0.001	
Horse Manure	<0.001	0.002	0.002	<0.001	0.006
Duplicate	<0.001	<0.001	<0.001		
Wood Chips	<0.001	0.011	<0.001	<0.001	0.007
Duplicate	<0.001			<0.001	
Treatment 2					
Cow Manure	<0.001	0.006	0.002	<0.001	0.007
Duplicate	<0.001	<0.001		<0.001	0.003
Straw	<0.001	0.001	0.002	<0.001	0.003
Duplicate	<0.001		0.002		0.003
Peat	<0.001	<0.001	0.002	<0.001	0.003
Duplicate	<0.001			<0.001	
Horse Manure	<0.001	0.023	<0.001	<0.001	0.002
Duplicate	<0.001	0.002	0.001		
Wood Chips	<0.001	0.001	<0.001	<0.001	0.002
Duplicate	<0.001			0.001	
Treatment 3					
Cow Manure	<0.001	0.292	0.048	0.028	0.361
Duplicate	<0.001	0.311		0.024	0.297
Straw	<0.001	0.273	0.046	0.022	0.302
Duplicate	<0.001		0.051		0.308
Peat	<0.001	0.325	0.067	0.042	0.467
Duplicate	<0.001			0.035	
Horse Manure	<0.001	0.362	0.026	0.019	0.19
Duplicate	<0.001	0.176	0.046		
Wood Chips	<0.001	0.189	0.031	0.031	0.226
Duplicate	<0.001			0.027	
Water Only	<0.001	<0.001	<0.001	<0.001	<0.001
Duplicate	<0.001	<0.001	<0.001		<0.001

Magnesium (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	178	176	165.8	160.7	190.4
Duplicate	178	169.4		132.2	114.3
Straw	178	249	170	181.1	166.5
Duplicate	178		152.6		196.2
Peat	178	126.1	82.6	90.3	93.5
Duplicate	178			84.8	
Horse Manure	178	162.2	162.7	130.6	142.2
Duplicate	178	154.4	153.9		
Wood Chips	178	142.1	107.3	104	107.2
Duplicate	178			99.2	
Treatment 2					
Cow Manure	178	192	161.7	158	173.4
Duplicate	178	176.9		152.5	167.7
Straw	178	260.4	180.8	179.5	218.2
Duplicate	178		155.7		223.3
Peat	178	122.5	86.4	87.9	91.04
Duplicate	178			76.9	
Horse Manure	178	190.2	156.3	153.5	141.1
Duplicate	178	170.9	191.8		
Wood Chips	178	179.1	124.2	126.7	102.6
Duplicate	178			121.6	
Treatment 3					
Cow Manure	178	276.2	222.8	135.6	383.8
Duplicate	178	315.5		172.1	326.5
Straw	178	359.2	216.1	224	325.1
Duplicate	178		218.7		318.3
Peat	178	264.9	173.7	172.2	278.1
Duplicate	178			182.8	
Horse Manure	178	263.5	187.1	193.9	303.8
Duplicate	178	237.1	186		
Wood Chips	178	254.6	164.4	175.8	236.6
Duplicate	178			173.7	
Water Only	178	183.4	145.3	143.8	167.3
Duplicate	178	173.3	143.1		169.9

Cells with no values indicate that a duplicate was not taken.

Manganese (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	0.1675	2.8323	8.48	3.619	2.485
Duplicate	0.1675	20.0983		0.7435	7.295
Straw	0.1675	2.2563	3.156	4.0525	1.062
Duplicate	0.1675		3.892		6.218
Peat	0.1675	12.6483	12.025	13.435	13.15
Duplicate	0.1675			13.675	
Horse Manure	0.1675	25.5483	2.519	1.2405	0.5983
Duplicate	0.1675	27.2183	2.5705		
Wood Chips	0.1675	16.5783	3.151	0.9635	0.6176
Duplicate	0.1675			0.9095	
Treatment 2					
Cow Manure	0.1675	2.5153	8.69	1.514	3.108
Duplicate	0.1675	2.4233		3.614	2.996
Straw	0.1675	1.4253	10.17	3.838	5.392
Duplicate	0.1675		3.1355		6.064
Peat	0.1675	11.6883	1.4305	4.2895	8.461
Duplicate	0.1675			6.38	
Horse Manure	0.1675	30.4583	2.4115	1.7135	0.5598
Duplicate	0.1675	17.4783	5.745		
Wood Chips	0.1675	41.6483	2.2105	1.2835	0.3305
Duplicate	0.1675			1.6605	
Treatment 3					
Cow Manure	0.1675	180.598	124.3	70.4	155.3
Duplicate	0.1675	174.098		83.1	157.2
Straw	0.1675	171.298	139.55	139.05	165.9
Duplicate	0.1675		136.15		143.4
Peat	0.1675	172.798	113.55	118.75	152.8
Duplicate	0.1675			140.1	
Horse Manure	0.1675	193.698	163.75	147.6	201.2
Duplicate	0.1675	141.698	163.65		
Wood Chips	0.1675	195.398	146.15	156.6	186.9
Duplicate	0.1675			153.05	
Water Only	0.1675	0.0117	0.1334	0.0957	0.119
Duplicate	0.1675	0.0034	0.0966		0.0791

Sodium (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	23.53	257.18	27.41	275.45	282.3
Duplicate	23.53	107.18		191.75	141.4
Straw	23.53	113.68	207.68	133.7	169.7
Duplicate	23.53		42.39		108.9
Peat	23.53	25.26	155.18	20.11	20
Duplicate	23.53			19.65	
Horse Manure	23.53	34.1	19.22	35.35	37.63
Duplicate	23.53	32.48	22.21		
Wood Chips	23.53	22.29	45.5	20.79	19.21
Duplicate	23.53			19.88	
Treatment 2					
Cow Manure	23.53	300.88	35.16	291.05	294.7
Duplicate	23.53	274.98		266.55	295
Straw	23.53	118.48	304.08	109.3	116
Duplicate	23.53		130.83		124.8
Peat	23.53	24.67	18.93	20.34	20.33
Duplicate	23.53			17.83	
Horse Manure	23.53	35.95	19.62	40.43	32.76
Duplicate	23.53	150.38	117.93		
Wood Chips	23.53	25.13	111.38	20.36	18.43
Duplicate	23.53			17.79	
Treatment 3					
Cow Manure	23.53	190.98	80.03	98.95	469
Duplicate	23.53	273.38		168.4	286.3
Straw	23.53	122.58	328.08	125.7	116.4
Duplicate	23.53		71.63		102.6
Peat	23.53	56.43	173.58	42.06	67.06
Duplicate	23.53			60.8	
Horse Manure	23.53	63.83	21.57	61.55	84.64
Duplicate	23.53	44.05	36.24		
Wood Chips	23.53	57.96	64.88	52.2	53.96
Duplicate	23.53			51.4	
Water Only	23.53	26.81	53.18	22.81	22.19
Duplicate	23.53	24.51	22.95		22.65

Cells with no values indicate that a duplicate was not taken.

Nickel (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	0.034	0.023	0.037	0.023	0.026
Duplicate	0.034	0.015		0.012	0.019
Straw	0.034	0.011	0.037	0.038	0.018
Duplicate	0.034		0.024		0.024
Peat	0.034	0.008	<0.002	0.007	0.004
Duplicate	0.034			0.006	
Horse Manure	0.034	0.007	0.007	0.012	0.017
Duplicate	0.034	0.009	0.013		
Wood Chips	0.034	0.004	<0.002	0.007	0.009
Duplicate	0.034			0.003	
Treatment 2					
Cow Manure	0.034	0.02	0.08	0.027	0.04
Duplicate	0.034	0.021		0.026	0.033
Straw	0.034	0.02	0.07	0.032	0.022
Duplicate	0.034		0.013		0.03
Peat	0.034	0.006	0.006	<0.002	0.017
Duplicate	0.034			0.004	
Horse Manure	0.034	0.009	0.009	0.026	0.018
Duplicate	0.034	0.016	0.023		
Wood Chips	0.034	0.049	0.008	0.006	0.008
Duplicate	0.034			0.005	
Treatment 3					
Cow Manure	0.034	0.947	0.576	0.35	0.593
Duplicate	0.034	0.931		0.378	0.704
Straw	0.034	0.797	0.692	0.72	0.776
Duplicate	0.034		0.692		0.654
Peat	0.034	0.789	0.387	0.376	0.469
Duplicate	0.034			0.469	
Horse Manure	0.034	1.05	0.887	0.821	1.016
Duplicate	0.034	0.765	0.92		
Wood Chips	0.034	1.087	0.903	1.041	1.072
Duplicate	0.034			1.024	
Water Only	0.034	0.042	0.032	0.028	0.036
Duplicate	0.034	0.028	0.035		0.038

Vanadium (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	<0.006	0.01	0.067	0.016	0.007
Duplicate	<0.006	<0.006		<0.006	0.007
Straw	<0.006	0.009	0.032	0.016	0.03
Duplicate	<0.006		0.028		0.008
Peat	<0.006	<0.006	<0.006	<0.006	<0.006
Duplicate	<0.006			<0.006	
Horse Manure	<0.006	<0.006	<0.006	0.013	<0.006
Duplicate	<0.006	<0.006	<0.006		
Wood Chips	<0.006	0.008	<0.006	<0.006	<0.006
Duplicate	<0.006			<0.006	
Treatment 2					
Cow Manure	<0.006	<0.006	0.027	0.009	0.007
Duplicate	<0.006	0.008		0.011	0.009
Straw	<0.006	<0.006	0.041	0.009	0.012
Duplicate	<0.006		<0.006		0.014
Peat	<0.006	<0.006	<0.006	<0.006	0.007
Duplicate	<0.006			<0.006	
Horse Manure	<0.006	<0.006	<0.006	0.009	<0.006
Duplicate	<0.006	<0.006	0.011		
Wood Chips	<0.006	0.013	<0.006	<0.006	0.011
Duplicate	<0.006			<0.006	
Treatment 3					
Cow Manure	<0.006	0.713	0.099	0.098	0.061
Duplicate	<0.006	0.569		0.053	0.057
Straw	<0.006	0.64	0.219	0.138	0.214
Duplicate	<0.006		0.138		0.13
Peat	<0.006	0.204	0.026	0.015	<0.006
Duplicate	<0.006			0.034	
Horse Manure	<0.006	0.483	0.124	0.055	0.075
Duplicate	<0.006	0.341	0.122		
Wood Chips	<0.006	0.617	0.51	0.503	0.407
Duplicate	<0.006			0.43	
Water Only	<0.006	<0.006	<0.006	<0.006	<0.006
Duplicate	<0.006	<0.006	<0.006		<0.006

Cells with no values indicate that a duplicate was not taken.

Zinc (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	0.003	0.054	0.196	0.033	0.033
Duplicate	0.003	0.014		0.019	0.034
Straw	0.003	0.054	0.125	0.135	0.072
Duplicate	0.003		0.071		0.036
Peat	0.003	0.01	0.002	0.01	0.007
Duplicate	0.003			0.003	
Horse Manure	0.003	0.009	0.016	0.021	0.035
Duplicate	0.003	0.009	0.015		
Wood Chips	0.003	0.015	0.001	0.004	0.018
Duplicate	0.003			0.005	
Treatment 2					
Cow Manure	0.003	0.1	0.22	0.071	0.074
Duplicate	0.003	0.064		0.097	0.067
Straw	0.003	0.089	0.33	0.09	0.078
Duplicate	0.003		0.022		0.119
Peat	0.003	0.008	0.002	0.005	0.011
Duplicate	0.003			0.005	
Horse Manure	0.003	0.02	0.021	0.069	0.031
Duplicate	0.003	0.051	0.089		
Wood Chips	0.003	0.045	0.007	0.011	0.006
Duplicate	0.003			0.011	
Treatment 3					
Cow Manure	0.003	2.428	1.698	0.942	1.815
Duplicate	0.003	3.366		0.666	1.122
Straw	0.003	6.259	3.337	2.472	2.335
Duplicate	0.003		2.251		2.145
Peat	0.003	0.847	0.246	0.203	0.212
Duplicate	0.003			0.335	
Horse Manure	0.003	1.44	1.437	1.186	1.446
Duplicate	0.003	1.168	1.26		
Wood Chips	0.003	1.451	0.544	0.858	0.781
Duplicate	0.003			0.666	
Water Only	0.003	0.023	0.024	0.01	0.008
Duplicate	0.003	0.009	0.008		0.02

Lead (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	<0.005	<0.005	0.016	<0.005	<0.005
Duplicate	<0.005	<0.005		<0.005	<0.005
Straw	<0.005	<0.005	<0.005	<0.005	<0.005
Duplicate	<0.005		<0.005		<0.005
Peat	<0.005	<0.005	<0.005	<0.005	<0.005
Duplicate	<0.005			<0.005	
Horse Manure	<0.005	0.011	<0.005	0.006	<0.005
Duplicate	<0.005	<0.005	<0.005		
Wood Chips	<0.005	<0.005	<0.005	<0.005	<0.005
Duplicate	<0.005			<0.005	
Treatment 2					
Cow Manure	<0.005	0.006	0.017	<0.005	<0.005
Duplicate	<0.005	<0.005		<0.005	<0.005
Straw	<0.005	<0.005	0.019	<0.005	<0.005
Duplicate	<0.005		<0.005		<0.005
Peat	<0.005	0.017	<0.005	<0.005	<0.005
Duplicate	<0.005			<0.005	
Horse Manure	<0.005	<0.005	<0.005	0.005	<0.005
Duplicate	<0.005	<0.005	<0.005		
Wood Chips	<0.005	0.027	<0.005	<0.005	<0.005
Duplicate	<0.005			0.006	
Treatment 3					
Cow Manure	<0.005	0.278	0.31	0.16	0.295
Duplicate	<0.005	0.059		0.161	0.32
Straw	<0.005	0.301	0.394	0.258	0.42
Duplicate	<0.005		0.336		0.302
Peat	<0.005	0.306	0.184	0.142	0.194
Duplicate	<0.005			0.257	
Horse Manure	<0.005	0.262	0.317	0.177	0.301
Duplicate	<0.005	0.174	0.295		
Wood Chips	<0.005	0.18	0.204	0.197	0.212
Duplicate	<0.005			0.204	
Water Only	<0.005	<0.005	<0.005	<0.005	<0.005
Duplicate	<0.005	0.006	<0.005		<0.005

Cells with no values indicate that a duplicate was not taken.

Sulphur (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	506.77	470.85	222.73	43.08	5.76
Duplicate	506.77	382.45		4.31	285.5
Straw	506.77	508.45	286.28	408.7	9.57
Duplicate	506.77		447.63		124.1
Peat	506.77	514.94	425.48	453.8	365.3
Duplicate	506.77			448.25	
Horse Manure	506.77	335.95	3.63	2.83	3.08
Duplicate	506.77	346.05	4.36		
Wood Chips	506.77	230.95	15.63	1.19	1.32
Duplicate	506.77			0.77	
Treatment 2					
Cow Manure	506.77	463.85	401.73	212.2	120.4
Duplicate	506.77	453.15		183.35	44.02
Straw	506.77	508.25	466.68	405.15	98.73
Duplicate	506.77		3.06		158.3
Peat	506.77	527.44	491.08	499.9	438.3
Duplicate	506.77			426.95	
Horse Manure	506.77	302.45	2.23	6.64	4.28
Duplicate	506.77	366.55	349.18		
Wood Chips	506.77	507.65	283.88	268	9.47
Duplicate	506.77			164.05	
Treatment 3					
Cow Manure	506.77	216.65	422.98	223.2	643
Duplicate	506.77	240.95		369.7	556.4
Straw	506.77	280.85	636.43	459.4	582.1
Duplicate	506.77		275.28		505.9
Peat	506.77	319.35	213.93	182.65	344.6
Duplicate	506.77			412.2	
Horse Manure	506.77	289.95	232.08	216.4	635.8
Duplicate	506.77	150.45	228.68		
Wood Chips	506.77	297.95	259.98	228.7	542.1
Duplicate	506.77			361.7	
Water Only	506.77	514.54	491.98	515	441.7
Duplicate	506.77	480.75	488.63		458.1

Potassium (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	6.46	1007.0	832.5	1191.5	1239.0
Duplicate	6.46	473.0		827.5	671.0
Straw	6.46	537.0	814.5	674.0	909.0
Duplicate	6.46		533.0		557.0
Peat	6.46	55.7.00	42.2	12.6	33.9
Duplicate	6.46			9.9	
Horse Manure	6.46	236.0	463.0	257.0	341.0
Duplicate	6.46	149.0	490.0		
Wood Chips	6.46	53.6	53.0	43.1	85.9
Duplicate	6.46			31.8	
Treatment 2					
Cow Manure	6.46	1342.0	1488.5	1355.5	1381.0
Duplicate	6.46	1096.0		1266.0	1389.0
Straw	6.46	663.0	540.0	538.0	640.0
Duplicate	6.46		416.0		742.0
Peat	6.46	12.4	28.9	12.1	9.3
Duplicate	6.46			12.1	
Horse Manure	6.46	358.0	421.0	565.0	388.0
Duplicate	6.46	718.0	650.0		
Wood Chips	6.46	162.0	53.5	68.5	37.0
Duplicate	6.46			51.0	
Treatment 3					
Cow Manure	6.46	3259.0	4128.0	1390.5	4996.0
Duplicate	6.46	3625.0		2006.5	3860.0
Straw	6.46	3031.0	3743.0	2838.5	2997.0
Duplicate	6.46		3161.0		2407.0
Peat	6.46	2390.0	2676.5	1788.0	3087.0
Duplicate	6.46			2569.0	
Horse Manure	6.46	2691.0	3293.0	2633.5	3644.0
Duplicate	6.46	2028.0	2807.5		
Wood Chips	6.46	2748.0	2425.5	2387.0	2542.0
Duplicate	6.46			2341.0	
Water Only	6.46	10.10	21.34	20.20	19.90
Duplicate	6.46	7.23	21.99		6.90

Cells with no values indicate that a duplicate was not taken.

Chromium (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	<0.002	0.007	0.03	0.006	0.009
Duplicate	<0.002	<0.002		0.003	0.023
Straw	<0.002	0.004	0.022	0.01	0.022
Duplicate	<0.002		0.006		0.011
Peat	<0.002	<0.002	<0.002	0.005	0.005
Duplicate	<0.002			<0.002	
Horse Manure	<0.002	<0.002	<0.002	0.005	0.011
Duplicate	<0.002	<0.002	<0.002		
Wood Chips	<0.002	0.002	<0.002	<0.002	<0.002
Duplicate	<0.002			0.003	
Treatment 2					
Cow Manure	<0.002	0.004	0.021	0.006	0.031
Duplicate	<0.002	0.007		0.007	0.027
Straw	<0.002	0.006	0.048	0.006	0.031
Duplicate	<0.002		<0.002		0.049
Peat	<0.002	0.003	<0.002	<0.002	0.031
Duplicate	<0.002			<0.002	
Horse Manure	<0.002	<0.002	<0.002	0.007	0.014
Duplicate	<0.002	0.004	0.006		
Wood Chips	<0.002	0.006	<0.002	0.003	0.01
Duplicate	<0.002			0.003	
Treatment 3					
Cow Manure	<0.002	0.459	0.343	0.138	1.422
Duplicate	<0.002	0.504		0.109	0.824
Straw	<0.002	0.535	0.445	0.228	1.525
Duplicate	<0.002		0.263		0.875
Peat	<0.002	0.433	0.074	0.065	1.338
Duplicate	<0.002			0.094	
Horse Manure	<0.002	0.433	0.272	0.149	1.182
Duplicate	<0.002	0.317	0.25		
Wood Chips	<0.002	0.327	0.326	0.34	2.085
Duplicate	<0.002			0.377	
Water Only	<0.002	<0.002	<0.002	<0.002	0.003
Duplicate	<0.002	<0.002	<0.002		<0.002

Iron (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	0.046	4.85	37.89	9.57	11.12
Duplicate	0.046	13.54		7.65	10.29
Straw	0.046	1.55	25.73	9.99	16.80
Duplicate	0.046		7.83		12.28
Peat	0.046	3.47	0.55	4.26	6.48
Duplicate	0.046			0.49	
Horse Manure	0.046	10.12	39.59	39.10	35.38
Duplicate	0.046	2.59	28.73		
Wood Chips	0.046	70.56	3.01	12.49	46.71
Duplicate	0.046			18.47	
Treatment 2					
Cow Manure	0.046	1.46	23.77	8.76	14.83
Duplicate	0.046	3.57		10.40	15.66
Straw	0.046	1.62	35.08	6.86	16.64
Duplicate	0.046		64.45		19.19
Peat	0.046	9.29	0.99	0.64	11.58
Duplicate	0.046			1.46	
Horse Manure	0.046	36.15	53.95	43.35	36.08
Duplicate	0.046	14.85	19.27		
Wood Chips	0.046	129.50	40.91	42.41	14.11
Duplicate	0.046			53.30	
Treatment 3					
Cow Manure	0.046	938.2	788.0	610.5	1086.0
Duplicate	0.046	1039.0		614.5	1048.0
Straw	0.046	1044.0	890.0	846.5	1405.0
Duplicate	0.046		844.5		1160.0
Peat	0.046	1094.0	497.0	510.0	654.1
Duplicate	0.046			756.5	
Horse Manure	0.046	984.8	811.5	596.5	1120.0
Duplicate	0.046	740.6	765.5		
Wood Chips	0.046	650.0	571.0	673.0	784.0
Duplicate	0.046			632.0	
Water Only	0.046	0.07	0.25	0.11	0.77
Duplicate	0.046	0.22	0.04		0.11

Cells with no values indicate that a duplicate was not taken.

Cobalt (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	<0.010	<0.010	<0.010	<0.010	<0.010
Duplicate	<0.010	<0.010		<0.010	<0.010
Straw	<0.010	<0.010	<0.010	<0.010	<0.010
Duplicate	<0.010		<0.010		<0.010
Peat	<0.010	0.01	<0.010	<0.010	<0.010
Duplicate	<0.010			<0.010	
Horse Manure	<0.010	<0.010	<0.010	<0.010	<0.010
Duplicate	<0.010	<0.010	<0.010		
Wood Chips	<0.010	<0.010	<0.010	<0.010	<0.010
Duplicate	<0.010			<0.010	
Treatment 2					
Cow Manure	<0.010	<0.010	<0.010	<0.010	<0.010
Duplicate	<0.010	<0.010		<0.010	<0.010
Straw	<0.010	<0.010	0.023	<0.010	<0.010
Duplicate	<0.010		<0.010		<0.010
Peat	<0.010	<0.010	<0.010	<0.010	<0.010
Duplicate	<0.010			<0.010	
Horse Manure	<0.010	<0.010	<0.010	<0.010	<0.010
Duplicate	<0.010	<0.010	<0.010		
Wood Chips	<0.010	<0.010	0.014	<0.010	<0.010
Duplicate	<0.010			<0.010	
Treatment 3					
Cow Manure	<0.010	<0.010	<0.010	<0.010	<0.010
Duplicate	<0.010	<0.010		<0.010	<0.010
Straw	<0.010	<0.010	<0.010	<0.010	<0.010
Duplicate	<0.010		<0.010		<0.010
Peat	<0.010	<0.010	<0.010	<0.010	<0.010
Duplicate	<0.010			<0.010	
Horse Manure	<0.010	<0.010	<0.010	<0.010	<0.010
Duplicate	<0.010	<0.010	<0.010		
Wood Chips	<0.010	0.125	<0.010	<0.010	0.016
Duplicate	<0.010			<0.010	
Water Only	<0.010	<0.010	<0.010	<0.010	<0.010
Duplicate	<0.010	<0.010	<0.010		<0.010

Alkalinity (as $CaCO_3$) - (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	122	500	1329	3931	2696
Duplicate	122	384		2065	1134
Straw	122	825	1292	3218	2696
Duplicate	122		1055		2350
Peat	122	315	130	514	476
Duplicate	122			451	
Horse Manure	122	552	1315	2283	1708
Duplicate	122	386	2076		
Wood Chips	122	597	695	1431	975
Duplicate	122			1427	
Treatment 2					
Cow Manure	122	335	1065	3558	2345
Duplicate	122	307		2325	2579
Straw	122	610	892	2738	2622
Duplicate	122		1746		2582
Peat	122	230	93	257	260
Duplicate	122			234	
Horse Manure	122	683	1121	3276	1599
Duplicate	122	452	2043		
Wood Chips	122	400	313	763	912
Duplicate	122			803	
Treatment 3					
Cow Manure	122	2751	N	8181	13908
Duplicate	122	2454		7228	15829
Straw	122	3248	N	10461	12371
Duplicate	122		N		12413
Peat	122	3285	N	15629	18364
Duplicate	122			14927	
Horse Manure	122	4567	N	14089	13690
Duplicate	122	3310	N		
Wood Chips	122	3409	N	11286	14762
Duplicate	122			12782	
Water Only	122	72	131	205	125
Duplicate	122	71	126		128

Cells with no values indicate that a duplicate was not taken.

pH

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	6.9	7.4	7.7	7.9	7.8
Duplicate	6.9	7.5		8.1	7.8
Straw	6.9	7.6	7.7	7.8	7.8
Duplicate	6.9		7.6		7.5
Peat	6.9	6.6	7.0	7.3	6.9
Duplicate	6.9			7.4	
Horse Manure	6.9	7.3	7.3	7.5	7.3
Duplicate	6.9	7.4	7.3		
Wood Chips	6.9	6.9	7.4	7.3	6.9
Duplicate	6.9			7.4	
Treatment 2					
Cow Manure	6.9	7.5	7.8	7.9	7.7
Duplicate	6.9	7.6		7.9	7.6
Straw	6.9	7.6	7.5	7.7	7.5
Duplicate	6.9		7.1		7.6
Peat	6.9	6.9	7.2	7.2	7.7
Duplicate	6.9			7.6	
Horse Manure	6.9	7.3	7.2	7.6	7.2
Duplicate	6.9	7.5	7.6		
Wood Chips	6.9	6.6	6.9	6.9	7.4
Duplicate	6.9			6.9	
Treatment 3					
Cow Manure	6.9	5.2	5.3	5.6	5.3
Duplicate	6.9	5.1		5.8	5.6
Straw	6.9	5.2	5.2	5.1	5.1
Duplicate	6.9		5.2		5.1
Peat	6.9	5.5	6.0	5.8	6.1
Duplicate	6.9			5.8	
Horse Manure	6.9	5.7	5.2	5.3	5.3
Duplicate	6.9	5.3	5.2		
Wood Chips	6.9	5.3	6.5	5.4	5.4
Duplicate	6.9			5.7	
Water Only	6.9	6.7	7.6	7.9	7.4
Duplicate	6.9	6.8	7.9		7.7

Chloride (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	12.88	530.8	<0.05	N	<0.05
Duplicate	12.88	216.14		N	<0.05
Straw	12.88	262.99	371.66	N	<0.05
Duplicate	12.88		N		238.99
Peat	12.88	63.43	N	N	49.07
Duplicate	12.88			N	
Horse Manure	12.88	76.86	64.1	N	52.39
Duplicate	12.88	32.9	N		
Wood Chips	12.88	22.16	73.82	N	66.05
Duplicate	12.88			N	
Treatment 2					
Cow Manure	12.88	819.53	<0.05	N	<0.05
Duplicate	12.88	576.75		N	<0.05
Straw	12.88	326.67	129.64	N	251.06
Duplicate	12.88		N		<0.05
Peat	12.88	24.77	106	N	21.83
Duplicate	12.88			N	
Horse Manure	12.88	84.04	160.97	N	87.75
Duplicate	12.88	298.27	N		
Wood Chips	12.88	95.61	66.08	N	21.84
Duplicate	12.88			N	
Treatment 3					
Cow Manure	12.88	N	N	N	N
Duplicate	12.88	N		N	N
Straw	12.88	N	N	N	N
Duplicate	12.88		N		N
Peat	12.88	N	N	N	N
Duplicate	12.88			N	
Horse Manure	12.88	N	N	N	N
Duplicate	12.88	N	N		
Wood Chips	12.88	N	N	N	N
Duplicate	12.88			N	
Water Only	12.88	15.89	46.19	N	19.94
Duplicate	12.88	12.98	39.62	N	19.06

Sulphide (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	<0.10	0.46	<0.10	0.2	<0.10
Duplicate	<0.10	0.3		0.16	<0.10
Straw	<0.10	0.28	<0.10	0.4	<0.10
Duplicate	<0.10		<0.10		<0.10
Peat	<0.10	<0.10	<0.10	<0.10	<0.10
Duplicate	<0.10			<0.10	
Horse Manure	<0.10	<0.10	<0.10	0.16	<0.10
Duplicate	<0.10	<0.10	<0.10		
Wood Chips	<0.10	<0.10	<0.10	<0.10	<0.10
Duplicate	<0.10	-		0.34	
Treatment 2					
Cow Manure	<0.10	0.97	<0.10	0.25	<0.10
Duplicate	<0.10	0.97		0.19	<0.10
Straw	<0.10	<0.10	0.11	0.23	<0.10
Duplicate	<0.10		<0.10		<0.10
Peat	<0.10	0.2	<0.10	<0.10	<0.10
Duplicate	<0.10			<0.10	
Horse Manure	<0.10	0.14	<0.10	0.2	<0.10
Duplicate	<0.10	1.01	<0.10		
Wood Chips	<0.10	0.4	<0.10	0.36	0.42
Duplicate	<0.10			<0.10	
Treatment 3					
Cow Manure	<0.10	N	N	N	N
Duplicate	<0.10	N	N	N	N
Straw	<0.10	N	N	N	N
Duplicate	<0.10	N	N	N	N
Peat	<0.10	N	N	N	N
Duplicate	<0.10	N	N	N	N
Horse Manure	<0.10	N	N	N	N
Duplicate	<0.10	N	N	N	N
Wood Chips	<0.10	N	N	N	N
Duplicate	<0.10	N	N	N	N
Water Only	<0.10	<0.10	<0.10	<0.10	<0.10
Duplicate	<0.10	<0.10	<0.10		<0.10

Cells with no values indicate that a duplicate was not taken. Cells with an N indicate that not enough water was available for analysis.

Barium (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	0.007	0.184	0.258	0.122	0.097
Duplicate	0.007	0.338		0.118	0.136
Straw	0.007	0.148	0.122	0.077	0.088
Duplicate	0.007		0.12		0.104
Peat	0.007	0.169	0.115	0.163	0.171
Duplicate	0.007			0.139	
Horse Manure	0.007	0.474	0.281	0.435	0.348
Duplicate	0.007	0.414	0.28		
Wood Chips	0.007	0.379	0.253	0.282	0.424
Duplicate	0.007			0.387	
Treatment 2					
Cow Manure	0.007	0.305	0.177	0.093	0.131
Duplicate	0.007	0.194		0.123	0.129
Straw	0.007	0.127	0.197	0.069	0.082
Duplicate	0.007		0.39		0.108
Peat	0.007	0.163	0.089	0.078	0.163
Duplicate	0.007			0.091	
Horse Manure	0.007	0.415	0.265	0.311	0.275
Duplicate	0.007	0.268	0.121		
Wood Chips	0.007	0.306	0.121	0.177	0.361
Duplicate	0.007			0.157	
Treatment 3					
Cow Manure	0.007	3.91	0.67	0.697	0.524
Duplicate	0.007	3.547		0.325	1.05
Straw	0.007	4.368	1.17	0.535	0.576
Duplicate	0.007		0.338		0.321
Peat	0.007	2.817	1.917	1.221	1.668
Duplicate	0.007			1.639	
Horse Manure	0.007	3.636	2.269	1.761	2.114
Duplicate	0.007	2.998	2.027		
Wood Chips	0.007	2.836	1.530	1.777	2.000
Duplicate	0.007			1.767	
Water Only	0.007	0.009	0.008	0.008	<0.003
Duplicate	0.007	0.008	0.008		<0.003

Cells with no values indicate that a duplicate was not taken.

Eh (mV)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	114.9	194.6	-235.5	-252.3	-268.6
Duplicate	114.9	-177.2		-235	-230.3
Straw	114.9	186.3	-286.4	-221	-282.6
Duplicate	114.9		-196.2		-233.5
Peat	114.9	-6.6	-27.6	-115.4	-101.7
Duplicate	114.9			-38.4	
Horse Manure	114.9	-142.5	-225.3	-138.5	-201.5
Duplicate	114.9	-133.3	-227		
Wood Chips	114.9	187.8	-224.3	-215.6	-144.4
Duplicate	114.9			-167.3	
Treatment 2					
Cow Manure	114.9	89.8	-261.2	-227.3	-198.5
Duplicate	114.9	-97.2		-199.6	-242
Straw	114.9	119.2	-242.5	-206	-247.1
Duplicate	114.9		-199.7		-249.5
Peat	114.9	117.5	55.8	14.6	N
Duplicate	114.9			-51	
Horse Manure	114.9	-211.1	-222	-161.8	-176.3
Duplicate	114.9	-62.6	-259		
Wood Chips	114.9	115.1	-227	-215.4	-193.5
Duplicate	114.9			-260	
Treatment 3					
Cow Manure	114.9	-102.2	-100.6	-67.4	31.3
Duplicate	114.9	-192.2		-125.5	-101.8
Straw	114.9	-137.2	-108.4	-63.8	-46.8
Duplicate	114.9		-122.6		-79.1
Peat	114.9	-157.2	-156.2	-102.3	-104.7
Duplicate	114.9			-94.6	
Horse Manure	114.9	-119.2	-64	-56.7	29.5
Duplicate	114.9	-147.1	-63.2		
Wood Chips	114.9	-188.6	-227.8	-75.4	-55.8
Duplicate	114.9			-66.7	
Water Only	114.9	193.1	122.5	136.1	266.7
Duplicate	114.9	197.7	146.5		242.4

Bicarbonate (mg/L)

Treatment	Initial	4 weeks	8 weeks	12 weeks	24 weeks
Treatment 1					
Cow Manure	121.6	498.74	1322.71	3897.58	2677.24
Duplicate	121.6	382.9		2035.3	1126.5
Straw	121.6	821.81	1284.79	3195.29	2678.13
Duplicate	121.6		1051.3		2341.9
Peat	121.6	314.4	129.4	512.9	475.1
Duplicate	121.6			450.1	
Horse Manure	121.6	550.9	1312.3	2274.9	1704.3
Duplicate	121.6	384.4	2071.5		
Wood Chips	121.6	596.4	692.8	1428.4	973.7
Duplicate	121.6			1422.6	
Treatment 2					
Cow Manure	121.6	334.0	1057.8	3523.1	2330.8
Duplicate	121.6	305.1		2302.9	2567.3
Straw	121.6	607.6	888.4	2722.1	2613.1
Duplicate	121.6		1743.9		2570.8
Peat	121.6	229.3	92.5	256.2	258.7
Duplicate	121.6			232.9	
Horse Manure	121.6	681.6	1118.6	3262.3	1596.1
Duplicate	121.6	449.8	2033.3		
Wood Chips	121.6	399.3	312.8	761.8	908.9
Duplicate	121.6			802.2	
Treatment 3					
Cow Manure	121.6	2751.0		8180.5	13907.7
Duplicate	121.6	2453.5		7227.6	15828.4
Straw	121.6	3247.9	N	10460.9	12370.8
Duplicate	121.6		N		12412.8
Peat	121.6	3284.4	N	15628.0	18361.8
Duplicate	121.6			14926.1	
Horse Manure	121.6	4566.8	N	14088.7	13689.7
Duplicate	121.6	3309.4	N		
Wood Chips	121.6	3408.4	N	11285.7	14761.6
Duplicate	121.6			12781.4	
Water Only	121.6	72.0	130.5	203.3	124.3
Duplicate	121.6	70.5	125.1		127.7

Cells with no values indicate that a duplicate was not taken. Cells with an N indicate that not enough water was available for analysis.

APPENDIX 4

FLOW-THROUGH REACTOR EXPERIMENT DATA

Conductivity (uS/cm)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Reactor 1	2301	2684	1992	1904	1835	2003	2149
Reactor 2	2301	2249	2151	2126	2153	2111	2119
Reactor 3	2301	2357	2094	2118	2174	2182	2168
Reactor 4	2301	2380	2026	2102	2106	2148	2094
Reactor 5	2301	2562	2303	1950	1965	1953	1983
Reactor 6	2301	2218	2095	2105	2144	2147	2066
Reactor 7	2301	1992	2199	2113	2086	2065	2089
Reactor 8	2301	2582	2298	2053	2063	2146	2134

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Reactor 1	2301	2223	2300	2305	2256	2320	1587
Reactor 2	2301	2069	2110	2102	2175	1968	1401
Reactor 3	2301	2084	2181	2087	2062	2161	1497
Reactor 4	2301	2135	2196	2124	2126	2244	1618
Reactor 5	2301	1960	2055	2064	2054	2162	1572
Reactor 6	2301	2043	2088	2020	2102	2027	1503
Reactor 7	2301	2011	2143	2017	2118	2034	1472
Reactor 8	2301	2134	2204	2085	2100	2180	1610

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Reactor 1	2301	2444	2621	2334	2354	2811
Reactor 2	2301	1939	2059	1971	2284	N
Reactor 3	2301	2003	2059	2048	2546	1810
Reactor 4	2301	2192	2110	2158	2156	2143
Reactor 5	2301	2099	2081	2076	2185	1790
Reactor 6	2301	1887	1851	2229	2422	N
Reactor 7	2301	1893	1918	2031	2391	2164
Reactor 8	2301	2053	2014	2051	2130	N

Cells with an N indicate that not enough water was available for analysis.

TDS (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Reactor 1	1132	1315	976	933	899	981	1053
Reactor 2	1132	1102	1054	1042	1055	1034	1038
Reactor 3	1132	1155	1026	1038	1065	1069	1062
Reactor 4	1132	1166	993	1030	1032	1053	1026
Reactor 5	1132	1255	1129	955	963	957	972
Reactor 6	1132	1087	1027	1031	1051	1052	1012
Reactor 7	1132	976	1077	1035	1022	1012	1024
Reactor 8	1132	1265	1126	1006	1011	1052	1046

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Reactor 1	1132	1089	1127	1129	1105	1137	778
Reactor 2	1132	1014	1034	1030	1066	964	686
Reactor 3	1132	1021	1069	1023	1010	1059	734
Reactor 4	1132	1046	1076	1041	1042	1100	793
Reactor 5	1132	960	1077	1011	1006	1060	770
Reactor 6	1132	1001	1023	990	1030	993	736
Reactor 7	1132	986	1050	988	1038	997	721
Reactor 8	1132	1045	1080	1022	1029	1068	789

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Reactor 1	1132	1198	1284	1144	1153	1377
Reactor 2	1132	950	1009	966	1119	N
Reactor 3	1132	982	1009	1003	1246	887
Reactor 4	1132	1074	1034	1057	1057	1050
Reactor 5	1132	1029	1020	1017	1071	877
Reactor 6	1132	925	907	1092	1187	N
Reactor 7	1132	928	940	995	1171	1060
Reactor 8	1132	1006	987	1008	1044	N

Aluminum (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	0.013	0.013	0.027	0.014	0.046	0.019	0.024
Reactor 1	0.013	0.061	0.342	0.119	0.100	0.068	0.091
Reactor 2	0.013	0.020	0.163	0.066	0.051	0.088	0.043
Reactor 3	0.013	0.126	0.739	0.036	0.035	0.059	0.039
Reactor 4	0.013	0.138	0.051	0.045	0.045	0.043	0.033
Reactor 5	0.013	0.132	0.237	0.037	0.024	0.039	0.040
Reactor 6	0.013	0.040	0.390	0.040	0.021	0.046	0.068
Reactor 7	0.013	0.027	0.064	0.069	0.071	0.050	0.049
Reactor 8	0.013	0.026	0.030	0.057	0.054	0.034	0.036
Treatment	**Initial**	**Week 7**	**Week 8**	**Week 9**	**Week 10**	**Week 11**	**Week 12**
Initial	0.013	0.028	0.026	0.023	0.009	0.017	0.019
Reactor 1	0.013	0.070	0.051	0.046	0.044	0.046	0.033
Reactor 2	0.013	0.067	0.037	0.032	0.045	0.026	0.035
Reactor 3	0.013	0.045	0.035	0.029	0.019	0.032	0.030
Reactor 4	0.013	0.040	0.034	0.030	0.013	0.021	0.035
Reactor 5	0.013	0.066	0.057	0.053	0.038	0.031	0.038
Reactor 6	0.013	0.078	0.055	0.035	0.033	0.026	0.034
Reactor 7	0.013	0.084	0.034	0.030	0.023	0.021	0.035
Reactor 8	0.013	0.090	0.046	0.044	0.022	0.029	0.065
Treatment	**Initial**	**Week 13**	**Week 14**	**Week 15**	**Week 16**	**Week 20**	
Initial	0.013	0.085	N	0.058	0.035	0.047	
Reactor 1	0.013	0.063	0.017	0.056	0.060	0.021	
Reactor 2	0.013	0.013	0.036	0.064	0.053	N	
Reactor 3	0.013	0.013	0.031	0.054	0.079	0.029	
Reactor 4	0.013	0.003	0.044	0.054	0.048	0.022	
Reactor 5	0.013	0.009	0.027	0.055	0.039	0.016	
Reactor 6	0.013	0.003	0.001	0.048	0.038	N	
Reactor 7	0.013	0.003	0.045	0.093	0.083	0.028	
Reactor 8	0.013	0.024	0.029	0.060	0.089	N	

Cells with an N indicate that not enough water was available for analysis.

Arsenic (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	<0.025	<0.025	<0.025	0.034	<0.025	<0.025	<0.025
Reactor 1	<0.025	0.022	<0.025	0.036	<0.025	<0.025	<0.025
Reactor 2	<0.025	<0.025	<0.025	0.034	<0.025	<0.025	<0.025
Reactor 3	<0.025	0.033	<0.025	0.031	<0.025	<0.025	<0.025
Reactor 4	<0.025	0.029	<0.025	0.053	<0.025	<0.025	<0.025
Reactor 5	<0.025	0.055	<0.025	0.049	<0.025	<0.025	<0.025
Reactor 6	<0.025	0.036	<0.025	0.036	<0.025	<0.025	<0.025
Reactor 7	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Reactor 8	<0.025	0.036	<0.025	<0.025	<0.025	<0.025	<0.025
Treatment	**Initial**	**Week 7**	**Week 8**	**Week 9**	**Week 10**	**Week 11**	**Week 12**
Initial	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Reactor 1	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Reactor 2	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Reactor 3	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Reactor 4	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Reactor 5	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Reactor 6	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Reactor 7	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Reactor 8	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Treatment	**Initial**	**Week 13**	**Week 14**	**Week 15**	**Week 16**	**Week 20**	
Initial	<0.025	<0.025	N	0.006	<0.025	<0.025	
Reactor 1	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	
Reactor 2	<0.025	<0.025	<0.025	<0.025	<0.025	N	
Reactor 3	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	
Reactor 4	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	
Reactor 5	<0.025	<0.025	0.028	<0.025	<0.025	<0.025	
Reactor 6	<0.025	<0.025	<0.025	<0.025	<0.025	N	
Reactor 7	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	
Reactor 8	<0.025	<0.025	<0.025	<0.025	<0.025	N	

Beryllium (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 1	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 2	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 3	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 4	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 5	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 6	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 7	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 8	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Initial	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 1	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 2	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 3	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 4	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 5	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 6	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 7	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 8	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Initial	<0.002	<0.002	N	<0.002	<0.002	<0.002
Reactor 1	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 2	<0.002	<0.002	<0.002	<0.002	<0.002	N
Reactor 3	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 4	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 5	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 6	<0.002	<0.002	<0.002	<0.002	<0.002	N
Reactor 7	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Reactor 8	<0.002	<0.002	<0.002	<0.002	<0.002	N

Calcium (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	319.99	319.99	311.184	316.298	313.7	317.49	303.20
Reactor 1	319.99	260.20	237.08	203.80	195.60	206.89	236.60
Reactor 2	319.99	273.40	240.68	249.40	267.50	241.09	241.50
Reactor 3	319.99	238.80	227.18	229.10	255.10	268.19	234.40
Reactor 4	319.99	257.10	199.88	237.50	248.50	273.69	234.70
Reactor 5	319.99	315.20	233.08	205.00	217.70	228.59	208.30
Reactor 6	319.99	280.10	218.68	232.70	252.20	254.09	221.00
Reactor 7	319.99	307.50	225.78	247.40	255.90	238.89	252.50
Reactor 8	319.99	269.00	234.78	232.40	244.00	254.79	237.90

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Initial	319.99	283.50	288.00	303.463	310.295	294.59	314.20
Reactor 1	319.99	256.50	261.60	296.26	275.50	290.99	271.70
Reactor 2	319.99	251.00	251.50	261.06	273.50	235.19	235.40
Reactor 3	319.99	257.90	264.90	267.96	245.00	269.59	255.70
Reactor 4	319.99	252.50	254.50	265.46	261.90	278.99	266.20
Reactor 5	319.99	232.90	252.10	267.06	247.70	266.39	249.40
Reactor 6	319.99	244.80	261.00	261.46	265.30	253.59	247.00
Reactor 7	319.99	242.20	253.60	258.86	269.00	250.39	245.70
Reactor 8	319.99	260.70	270.00	266.56	253.60	273.69	270.50

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Initial	319.99	312.28	N	314.80	318.70	301.40
Reactor 1	319.99	267.68	277.17	266.20	280.00	254.20
Reactor 2	319.99	222.48	246.67	240.90	268.70	N
Reactor 3	319.99	234.88	246.07	249.90	232.20	217.50
Reactor 4	319.99	268.38	255.07	252.10	269.80	243.30
Reactor 5	319.99	260.88	261.77	246.80	249.80	194.40
Reactor 6	319.99	221.58	206.87	270.70	276.30	N
Reactor 7	319.99	219.08	237.17	244.20	266.70	255.00
Reactor 8	319.99	239.28	242.87	244.80	247.20	N

Cells with an N indicate that not enough water was available for analysis.

Cadmium (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 2	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 3	<0.001	<0.001	<0.001	0.002	<0.001	<0.001	<0.001
Reactor 4	<0.001	0.0040	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 5	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 6	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 7	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 8	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Treatment	**Initial**	**Week 7**	**Week 8**	**Week 9**	**Week 10**	**Week 11**	**Week 12**
Initial	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 2	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 3	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 4	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 5	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 6	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 7	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 8	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Treatment	**Initial**	**Week 13**	**Week 14**	**Week 15**	**Week 16**	**Week 20**	
Initial	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	
Reactor 1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	
Reactor 2	<0.001	<0.001	<0.001	<0.001	<0.001	N	
Reactor 3	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	
Reactor 4	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	
Reactor 5	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	
Reactor 6	<0.001	<0.001	<0.001	<0.001	<0.001	N	
Reactor 7	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	
Reactor 8	<0.001	<0.001	<0.001	<0.001	<0.001	N	

Cells with an N indicate that not enough water was available for analysis.

Magnesium (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	173.2	173.2	168.9	169.5	170	173.5	166.7
Reactor 1	173.2	128.3	126.3	119.5	120.3	130.9	140.7
Reactor 2	173.2	143.4	136.2	143.7	151.9	138.2	140.6
Reactor 3	173.2	126.5	129.2	134.4	147.3	151.8	136.8
Reactor 4	173.2	131.2	115.8	140.5	145.2	155.3	137.4
Reactor 5	173.2	143.6	125.0	120.3	133.9	137.5	125.6
Reactor 6	173.2	145.4	125.8	136.2	145.5	144.8	128.4
Reactor 7	173.2	155.0	129.5	146.0	149.2	137.1	145.6
Reactor 8	173.2	135.2	129.7	138.3	145.2	147.5	139.1
Treatment	**Initial**	**Week 7**	**Week 8**	**Week 9**	**Week 10**	**Week 11**	**Week 12**
Initial	173.2	156.4	156.7	164.3	168.1	161.2	172.8
Reactor 1	173.2	147.4	146.8	163.4	152.6	160.1	153.6
Reactor 2	173.2	143.9	141.7	146.1	152.1	133.3	135.9
Reactor 3	173.2	147.3	148.4	149.3	138.0	150.2	146.2
Reactor 4	173.2	145.6	144.3	149.2	146.7	155.2	151.9
Reactor 5	173.2	137.1	144.2	150.8	140.3	148.9	142.7
Reactor 6	173.2	140.3	146.9	146.3	148.4	142.1	141.9
Reactor 7	173.2	139.8	144.0	145.4	150.4	140.8	141.5
Reactor 8	173.2	148.6	151.3	148.7	142.6	152.8	154.0
Treatment	**Initial**	**Week 13**	**Week 14**	**Week 15**	**Week 16**	**Week 20**	
Initial	173.2	172.69	N	172.3	177.4	174.1	
Reactor 1	173.2	151.6	157.5	151.9	161.0	151.9	
Reactor 2	173.2	129.7	143.3	139.2	155.4	N	
Reactor 3	173.2	135.8	142.9	144.3	136.5	133.7	
Reactor 4	173.2	153.1	147.9	145.5	156.8	144.6	
Reactor 5	173.2	148.9	150.7	142.9	146.2	119.5	
Reactor 6	173.2	129.2	122.5	154.7	158.9	N	
Reactor 7	173.2	127.7	138.6	142.4	154.3	152.2	
Reactor 8	173.2	138.4	141.2	142.2	145.3	N	

Manganese (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	0.0608	0.0608	0.0506	0.0395	0.0331	0.0227	0.0006
Reactor 1	0.0608	10.760	7.9630	5.4040	5.1200	3.6850	2.1230
Reactor 2	0.0608	12.970	5.4190	4.0310	2.4720	1.8400	1.2970
Reactor 3	0.0608	10.370	7.8950	4.0620	2.6660	1.9430	1.0790
Reactor 4	0.0608	12.230	6.4390	4.2900	2.3350	1.5270	0.8430
Reactor 5	0.0608	18.550	10.5200	7.8430	6.0390	3.7260	2.3980
Reactor 6	0.0608	11.240	5.4010	3.6560	2.4850	1.7010	1.1590
Reactor 7	0.0608	15.760	5.8740	3.9520	2.2910	1.3420	1.0520
Reactor 8	0.0608	11.500	8.1250	5.4520	3.6290	1.9990	1.2850
Treatment	**Initial**	**Week 7**	**Week 8**	**Week 9**	**Week 10**	**Week 11**	**Week 12**
Initial	0.0608	0.0173	<0.0002	<0.0002	<0.0002	<0.0002	0.0012
Reactor 1	0.0608	1.5870	1.2410	1.1530	0.9370	0.8820	0.7930
Reactor 2	0.0608	1.1120	0.9370	0.8660	0.8530	0.6690	0.6530
Reactor 3	0.0608	0.9760	0.8660	0.7430	0.6570	0.6680	0.6340
Reactor 4	0.0608	0.7730	0.7020	0.6400	0.5950	0.5940	0.5610
Reactor 5	0.0608	2.2160	1.8700	1.7030	1.4040	1.1660	0.9720
Reactor 6	0.0608	1.1140	0.9190	0.8630	0.8240	0.6820	0.6640
Reactor 7	0.0608	0.8360	0.7440	0.6670	0.6560	0.5700	0.5510
Reactor 8	0.0608	1.0500	0.8750	0.7410	0.6300	0.6400	0.6120
Treatment	**Initial**	**Week 13**	**Week 14**	**Week 15**	**Week 16**	**Week 20**	
Initial	0.0608	0.0003	N	0.0767	0.0757	0.0469	
Reactor 1	0.0608	0.7840	0.7450	0.7000	0.7200	0.4600	
Reactor 2	0.0608	0.6140	0.6740	0.6070	0.7010	N	
Reactor 3	0.0608	0.5840	0.5730	0.5820	0.5240	0.5200	
Reactor 4	0.0608	0.5630	0.5220	0.4970	0.5280	0.5780	
Reactor 5	0.0608	0.9690	0.8930	0.7870	0.6970	0.5590	
Reactor 6	0.0608	0.5890	0.5170	0.6210	0.5980	N	
Reactor 7	0.0608	0.5000	0.5220	0.5100	0.5340	0.5280	
Reactor 8	0.0608	0.5470	0.5320	0.5530	0.6060	N	

Cells with an N indicate that not enough water was available for analysis.

Sodium (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	23.58	23.58	22.76	22.94	24.03	27.08	22.30
Reactor 1	23.58	31.41	25.26	21.47	20.56	25.45	21.99
Reactor 2	23.58	21.77	19.26	20.86	23.36	19.69	18.54
Reactor 3	23.58	22.85	19.67	19.80	26.63	22.05	18.06
Reactor 4	23.58	26.70	18.56	20.53	22.67	22.81	17.86
Reactor 5	23.58	36.80	24.63	20.69	21.22	20.81	16.68
Reactor 6	23.58	28.45	18.77	19.32	23.50	20.89	16.44
Reactor 7	23.58	33.85	21.21	21.38	22.82	19.40	19.02
Reactor 8	23.58	24.53	21.22	20.68	22.91	22.33	18.29
Treatment	**Initial**	**Week 7**	**Week 8**	**Week 9**	**Week 10**	**Week 11**	**Week 12**
Initial	23.58	21.15	21.59	21.53	22.16	21.23	23.43
Reactor 1	23.58	20.69	19.58	21.96	21.05	21.92	20.08
Reactor 2	23.58	19.29	18.84	20.45	19.85	17.16	17.35
Reactor 3	23.58	20.34	19.98	20.08	18.10	19.73	18.87
Reactor 4	23.58	19.57	18.92	19.53	19.18	20.28	19.57
Reactor 5	23.58	18.95	19.66	20.32	18.04	19.47	18.54
Reactor 6	23.58	18.81	20.28	18.91	19.61	19.01	18.07
Reactor 7	23.58	18.66	19.46	18.62	19.86	17.93	17.91
Reactor 8	23.58	20.28	20.22	19.41	18.42	20.02	20.01
Treatment	**Initial**	**Week 13**	**Week 14**	**Week 15**	**Week 16**	**Week 20**	
Initial	23.58	23.66	N	27.90	30.87	30.63	
Reactor 1	23.58	20.09	20.53	20.14	23.60	23.20	
Reactor 2	23.58	16.30	18.25	18.21	22.79	N	
Reactor 3	23.58	17.37	18.03	19.11	19.36	20.23	
Reactor 4	23.58	19.68	18.86	19.15	22.75	23.20	
Reactor 5	23.58	19.12	19.30	18.66	20.87	17.59	
Reactor 6	23.58	16.16	14.97	21.13	23.50	N	
Reactor 7	23.58	15.83	17.27	19.00	22.41	23.34	
Reactor 8	23.58	17.62	17.77	18.54	20.63	N	

Nickel (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	0.035	0.035	0.034	0.031	0.024	0.027	0.024
Reactor 1	0.035	0.007	0.001	0.008	0.001	0.002	0.001
Reactor 2	0.035	0.003	0.001	0.007	0.001	0.001	0.004
Reactor 3	0.035	0.001	0.001	0.004	0.004	0.001	0.006
Reactor 4	0.035	0.009	0.001	0.010	0.001	0.001	0.004
Reactor 5	0.035	0.004	0.001	0.005	0.001	0.003	0.001
Reactor 6	0.035	0.001	0.004	0.011	0.008	0.001	0.007
Reactor 7	0.035	0.007	0.004	0.012	0.001	0.005	0.005
Reactor 8	0.035	0.013	0.001	0.013	0.001	0.001	0.007

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Initial	0.035	0.026	0.019	0.023	0.023	0.028	0.021
Reactor 1	0.035	0.001	0.001	0.001	0.005	0.004	0.001
Reactor 2	0.035	0.001	0.001	0.001	0.001	0.004	0.001
Reactor 3	0.035	0.001	0.001	0.005	0.002	0.002	0.001
Reactor 4	0.035	0.001	0.004	0.001	0.001	0.003	0.001
Reactor 5	0.035	0.001	0.001	0.002	0.001	0.005	0.001
Reactor 6	0.035	0.003	0.001	0.001	0.001	0.005	0.001
Reactor 7	0.035	0.001	0.001	0.001	0.001	0.002	0.002
Reactor 8	0.035	0.007	0.001	0.003	0.001	0.005	0.001

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Initial	0.035	0.023	N	0.025	0.030	0.026
Reactor 1	0.035	0.001	0.004	0.001	0.004	0.002
Reactor 2	0.035	0.001	0.001	0.002	0.002	N
Reactor 3	0.035	0.001	0.001	0.001	0.004	0.004
Reactor 4	0.035	0.001	0.001	0.001	0.002	0.004
Reactor 5	0.035	0.001	0.001	0.001	0.001	0.004
Reactor 6	0.035	0.001	0.001	0.001	0.001	N
Reactor 7	0.035	0.001	0.004	0.003	0.001	0.008
Reactor 8	0.035	0.001	0.001	0.001	0.001	N

Cells with an N indicate that not enough water was available for analysis.

Vanadium (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 3	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 4	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 5	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 6	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 7	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 8	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Initial	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 3	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 4	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 5	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 6	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 7	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 8	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Initial	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 2	<0.05	<0.05	<0.05	<0.05	<0.05	N
Reactor 3	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 4	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 5	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 6	<0.05	<0.05	<0.05	<0.05	<0.05	N
Reactor 7	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Reactor 8	<0.05	<0.05	<0.05	<0.05	<0.05	N

Sulphur (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	507.4	507.4	487.9	515.5	504.2	517.7	489.8
Reactor 1	507.4	314.9	266.1	85.4	56.1	90.8	202.6
Reactor 2	507.4	374.4	302.6	275.6	334.4	270.1	279.2
Reactor 3	507.4	300.3	244.4	231.1	279.5	255.5	252.4
Reactor 4	507.4	325.1	241.6	264.6	288.8	300.2	260.3
Reactor 5	507.4	311.5	230.1	138.0	203.7	190.3	181.8
Reactor 6	507.4	362.2	278.1	271.4	297.2	294.3	248.3
Reactor 7	507.4	395.8	324.2	260.6	281.3	256.4	270.6
Reactor 8	507.4	344.4	302.2	249.1	256.0	262.1	242.3
Treatment	**Initial**	**Week 7**	**Week 8**	**Week 9**	**Week 10**	**Week 11**	**Week 12**
Initial	507.4	457.7	475.44	488.34	504.23	483.69	513.2
Reactor 1	507.4	257.4	300.5	335.0	335.5	366.1	325.8
Reactor 2	507.4	296.5	322.4	315.6	339.6	297.9	304.2
Reactor 3	507.4	279.3	325.2	302.2	291.6	347.6	313.5
Reactor 4	507.4	275.2	305.4	297.5	313.6	347.6	335.0
Reactor 5	507.4	178.4	209.1	207.7	227.7	291.0	297.9
Reactor 6	507.4	273.7	321.7	293.4	313.4	307.9	307.3
Reactor 7	507.4	238.4	293.2	281.9	308.4	293.6	294.5
Reactor 8	507.4	273.6	314.2	285.7	284.4	298.5	309.7
Treatment	**Initial**	**Week 13**	**Week 14**	**Week 15**	**Week 16**	**Week 20**	
Initial	507.4	512	N	505.6	526.5	528.7	
Reactor 1	507.4	339.6	349.3	342.5	378.9	327.4	
Reactor 2	507.4	295.7	325.2	318.3	386.4	N	
Reactor 3	507.4	304.1	311.8	321.5	311.6	296.5	
Reactor 4	507.4	345.4	326.0	326.6	359.4	329.1	
Reactor 5	507.4	335.5	332.6	323.4	340.0	262.2	
Reactor 6	507.4	288.4	261.6	365.4	398.0	N	
Reactor 7	507.4	279.5	292.6	312.9	359.0	332.5	
Reactor 8	507.4	291.6	288.5	306.5	323.9	N	

Cells with an N indicate that not enough water was available for analysis.

Copper (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Reactor 1	<0.005	<0.005	<0.005	<0.005	0.007	0.007	<0.005
Reactor 2	<0.005	<0.005	0.008	<0.005	<0.005	0.003	<0.005
Reactor 3	<0.005	<0.005	0.015	<0.005	<0.005	<0.005	<0.005
Reactor 4	<0.005	0.008	<0.005	<0.005	<0.005	<0.005	<0.005
Reactor 5	<0.005	0.007	<0.005	<0.005	0.006	<0.005	<0.005
Reactor 6	<0.005	<0.005	0.008	<0.005	0.013	0.006	<0.005
Reactor 7	<0.005	0.007	0.016	<0.005	0.009	<0.005	<0.005
Reactor 8	<0.005	<0.005	<0.005	<0.005	0.008	0.006	<0.005
Treatment	**Initial**	**Week 7**	**Week 8**	**Week 9**	**Week 10**	**Week 11**	**Week 12**
Initial	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Reactor 1	<0.005	<0.005	<0.005	<0.005	0.008	<0.005	<0.005
Reactor 2	<0.005	<0.005	<0.005	<0.005	0.003	<0.005	<0.005
Reactor 3	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Reactor 4	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Reactor 5	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Reactor 6	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Reactor 7	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Reactor 8	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Treatment	**Initial**	**Week 13**	**Week 14**	**Week 15**	**Week 16**	**Week 20**	
Initial	<0.005	<0.005	N	<0.005	<0.005	<0.005	
Reactor 1	<0.005	0.006	<0.005	<0.005	<0.005	<0.005	
Reactor 2	<0.005	<0.005	<0.005	<0.005	<0.005	N	
Reactor 3	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	
Reactor 4	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	
Reactor 5	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	
Reactor 6	<0.005	<0.005	<0.005	0.007	<0.005	N	
Reactor 7	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	
Reactor 8	<0.005	<0.005	<0.005	<0.005	<0.005	N	

Potassium (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	6.81	6.81	6.75	6.62	6.87	7.11	6.46
Reactor 1	6.81	127.00	71.60	55.10	30.40	19.80	9.39
Reactor 2	6.81	42.30	22.50	13.90	11.20	7.54	6.36
Reactor 3	6.81	64.80	41.40	12.70	11.20	7.78	6.13
Reactor 4	6.81	96.10	38.50	13.70	9.65	7.88	6.01
Reactor 5	6.81	146.00	76.10	40.50	17.50	9.59	6.46
Reactor 6	6.81	73.60	21.90	11.00	8.41	7.28	5.55
Reactor 7	6.81	132.00	24.00	14.50	8.68	7.28	6.60
Reactor 8	6.81	79.40	57.10	18.40	10.70	7.97	6.46
Treatment	**Initial**	**Week 7**	**Week 8**	**Week 9**	**Week 10**	**Week 11**	**Week 12**
Initial	6.81	6.05	7.13	0.05	0.05	6.16	6.89
Reactor 1	6.81	7.11	7.54	0.05	0.05	9.62	10.10
Reactor 2	6.81	5.92	6.08	0.05	0.05	6.91	7.42
Reactor 3	6.81	6.46	6.78	0.05	0.05	7.70	7.18
Reactor 4	6.81	6.15	6.16	0.05	0.05	6.40	7.35
Reactor 5	6.81	6.73	7.76	0.05	0.05	6.26	6.88
Reactor 6	6.81	6.40	6.48	0.05	0.05	6.54	12.60
Reactor 7	6.81	5.47	6.11	0.05	0.05	5.72	7.54
Reactor 8	6.81	6.52	6.54	0.05	0.05	6.84	7.59
Treatment	**Initial**	**Week 13**	**Week 14**	**Week 15**	**Week 16**	**Week 20**	
Initial	6.81	6.85	N	6.49	22.6	7.41	
Reactor 1	6.81	60.80	98.30	25.90	17.10	6.57	
Reactor 2	6.81	7.24	19.80	7.02	8.68	N	
Reactor 3	6.81	5.99	6.34	6.38	157.00	9.42	
Reactor 4	6.81	7.59	6.62	6.27	6.12	168.00	
Reactor 5	6.81	6.29	7.04	5.92	9.25	4.91	
Reactor 6	6.81	6.02	5.30	11.20	6.60	N	
Reactor 7	6.81	5.26	5.84	12.10	6.40	7.62	
Reactor 8	6.81	5.84	5.68	5.52	5.48	N	

Cells with an N indicate that not enough water was available for analysis.

Total Metals (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	0.20	0.20	0.233	0.173	0.22	0.157	0.15
Reactor 1	0.20	91.24	43.93	13.71	25.48	6.06	4.35
Reactor 2	0.20	54.72	34.80	14.48	3.38	3.19	2.10
Reactor 3	0.20	91.08	68.10	15.34	3.58	3.75	2.17
Reactor 4	0.20	136.93	28.49	23.38	4.20	4.29	1.47
Reactor 5	0.20	195.44	34.14	23.79	7.62	8.71	5.82
Reactor 6	0.20	82.51	27.34	7.84	3.91	5.99	5.44
Reactor 7	0.20	59.44	40.42	19.87	4.91	6.33	2.52
Reactor 8	0.20	104.06	31.66	9.36	5.79	6.72	8.19
Treatment	**Initial**	**Week 7**	**Week 8**	**Week 9**	**Week 10**	**Week 11**	**Week 12**
Initial	0.20	0.18	N	N	N	N	0.15
Reactor 1	0.20	2.91	2.59	1.88	1.44	1.38	1.20
Reactor 2	0.20	2.02	1.49	1.27	1.24	0.98	1.00
Reactor 3	0.20	1.88	N	1.27	1.01	1.05	0.94
Reactor 4	0.20	2.43	1.23	1.18	0.95	0.95	0.88
Reactor 5	0.20	7.49	4.68	3.00	1.94	1.57	1.35
Reactor 6	0.20	3.05	1.64	1.31	1.21	0.99	0.96
Reactor 7	0.20	1.62	1.29	1.14	1.04	0.88	0.86
Reactor 8	0.20	7.90	3.92	2.24	1.10	1.05	1.03
Treatment	**Initial**	**Week 13**	**Week 14**	**Week 15**	**Week 16**	**Week 20**	
Initial	0.20	0.22	N	0.26	0.25	0.22	
Reactor 1	0.20	1.25	1.12	1.01	1.08	0.98	
Reactor 2	0.20	0.88	0.93	0.92	0.99	N	
Reactor 3	0.20	0.86	0.85	0.87	0.94	1.11	
Reactor 4	0.20	0.89	0.85	0.81	0.80	0.91	
Reactor 5	0.20	1.32	1.22	1.11	1.03	0.98	
Reactor 6	0.20	0.81	0.73	0.90	0.84	N	
Reactor 7	0.20	0.72	0.80	0.88	0.83	0.94	
Reactor 8	0.20	0.87	0.80	0.89	0.94	N	

Chromium (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 1	<0.001	<0.001	<0.001	0.002	<0.001	<0.001	0.003
Reactor 2	<0.001	<0.001	<0.001	0.002	<0.001	0.003	<0.001
Reactor 3	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 4	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.002
Reactor 5	<0.001	0.007	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 6	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 7	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 8	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Initial	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.003
Reactor 1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.002
Reactor 2	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.002
Reactor 3	<0.001	0.002	0.002	<0.001	<0.001	<0.001	<0.001
Reactor 4	<0.001	<0.001	0.002	<0.001	<0.001	<0.001	<0.001
Reactor 5	<0.001	<0.001	0.003	0.002	<0.001	<0.001	<0.001
Reactor 6	<0.001	0.002	<0.001	<0.001	<0.001	0.002	<0.001
Reactor 7	<0.001	<0.001	0.002	<0.001	<0.001	<0.001	0.003
Reactor 8	<0.001	<0.001	0.002	<0.001	<0.001	<0.001	<0.001

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Initial	<0.001	<0.001	<0.001	<0.001	<0.001	0.002
Reactor 1	<0.001	0.003	0.002	<0.001	<0.001	0.002
Reactor 2	<0.001	<0.001	<0.001	<0.001	<0.001	N
Reactor 3	<0.001	0.006	<0.001	<0.001	<0.001	0.002
Reactor 4	<0.001	<0.001	<0.001	<0.001	<0.001	0.003
Reactor 5	<0.001	<0.001	0.003	<0.001	<0.001	<0.001
Reactor 6	<0.001	0.002	<0.001	<0.001	<0.001	N
Reactor 7	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Reactor 8	<0.001	<0.001	0.002	0.003	<0.001	N

Cells with an N indicate that not enough water was available for analysis.

Iron (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	<0.005	0.005	0.020	<0.005	0.011	0.005	0.011
Reactor 1	<0.005	79.650	35.090	7.804	19.860	1.989	1.697
Reactor 2	<0.005	41.210	28.820	10.040	0.579	0.940	0.489
Reactor 3	<0.005	79.790	58.750	10.920	0.584	1.337	0.763
Reactor 4	<0.005	123.500	21.590	18.600	1.507	2.292	0.294
Reactor 5	<0.005	175.400	22.920	15.630	1.324	4.592	3.025
Reactor 6	<0.005	70.580	21.150	3.869	1.124	3.933	3.857
Reactor 7	<0.005	42.840	33.950	15.530	2.265	4.570	1.038
Reactor 8	<0.005	91.860	23.070	3.576	1.874	4.382	6.522

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Initial	<0.005	<0.005	<0.005	0.028	0.005	0.005	0.014
Reactor 1	<0.005	0.886	0.967	0.336	0.145	0.165	0.105
Reactor 2	<0.005	0.565	0.278	0.141	0.099	0.089	0.121
Reactor 3	<0.005	0.575	0.704	0.244	0.105	0.125	0.072
Reactor 4	<0.005	1.334	0.230	0.260	0.107	0.103	0.068
Reactor 5	<0.005	4.799	2.289	0.761	0.095	0.071	0.061
Reactor 6	<0.005	1.525	0.391	0.160	0.093	0.057	0.047
Reactor 7	<0.005	0.413	0.243	0.197	0.117	0.071	0.065
Reactor 8	<0.005	6.356	2.568	1.056	0.198	0.133	0.117

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Initial	<0.005	0.015	N	<0.005	0.013	0.007
Reactor 1	<0.005	0.138	0.111	0.038	0.089	0.336
Reactor 2	<0.005	0.091	0.045	0.077	0.057	N
Reactor 3	<0.005	0.071	0.052	0.051	0.156	0.373
Reactor 4	<0.005	0.125	0.077	0.079	0.051	0.110
Reactor 5	<0.005	0.079	0.033	0.047	0.094	0.229
Reactor 6	<0.005	0.039	0.030	0.032	0.028	N
Reactor 7	<0.005	0.040	0.034	0.076	0.035	0.194
Reactor 8	<0.005	0.088	0.031	0.071	0.041	N

Cobalt (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 5	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 6	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 7	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 8	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Initial	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 5	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 6	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 7	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 8	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Initial	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 2	<0.01	<0.01	<0.01	<0.01	<0.01	N
Reactor 3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 5	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 6	<0.01	<0.01	<0.01	<0.01	<0.01	N
Reactor 7	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Reactor 8	<0.01	<0.01	<0.01	<0.01	<0.01	N

Cells with an N indicate that not enough water was available for analysis.

Alkalinity (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	150.1	150.1	147.1	161.6	148.5	142	143.1
Reactor 1	150.1	402.2	431.4	1343.0	1093.0	914.4	772.8
Reactor 2	150.1	367.3	373.2	557.6	406.1	457.4	509.7
Reactor 3	150.1	381.2	499.8	671.9	539.4	630.9	581.1
Reactor 4	150.1	406.6	370.8	570.3	479.2	539.3	521.8
Reactor 5	150.1	655.0	595.8	814.1	615.2	649.8	690.0
Reactor 6	150.1	400.4	375.6	516.6	496.1	517.1	462.4
Reactor 7	150.1	487.0	270.4	627.1	559.7	536.6	545.2
Reactor 8	150.1	460.3	374.4	603.3	592.8	610.3	601.4

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Initial	150.1	N	155.4	151.4	149	143.5	147.4
Reactor 1	150.1	N	581.3	630.3	510.0	527.5	503.8
Reactor 2	150.1	N	436.7	469.5	493.0	415.8	379.8
Reactor 3	150.1	N	507.6	568.7	482.0	507.5	465.9
Reactor 4	150.1	N	501.4	562.9	N	503.6	473.2
Reactor 5	150.1	N	741.1	841.9	725.0	620.2	511.7
Reactor 6	150.1	N	469.9	549.4	531.0	461.3	426.2
Reactor 7	150.1	N	579.2	584.7	552.0	515.3	485.9
Reactor 8	150.1	N	563.3	576.7	532.0	623.1	555.8

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Initial	150.1	132.2	N	144.8	144.8	129.2
Reactor 1	150.1	421.2	468.0	434.3	387.3	450.1
Reactor 2	150.1	338.6	391.1	675.9	331.0	N
Reactor 3	150.1	363.1	423.9	384.5	N	401.9
Reactor 4	150.1	391.6	391.0	429.8	416.8	509.3
Reactor 5	150.1	403.3	435.8	372.8	388.8	355.7
Reactor 6	150.1	346.9	375.5	403.3	354.3	N
Reactor 7	150.1	352.0	552.1	412.5	421.0	414.4
Reactor 8	150.1	443.4	434.2	N	389.5	N

pH

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Reactor 1	7.9	7.0	6.7	7.7	7.6	7.5	7.5
Reactor 2	7.9	7.1	7.1	7.5	7.8	7.9	7.8
Reactor 3	7.9	7.1	7.0	7.2	7.7	7.8	7.6
Reactor 4	7.9	7.1	6.9	7.2	7.5	7.8	7.5
Reactor 5	7.9	7.3	7.1	7.3	7.6	7.9	7.6
Reactor 6	7.9	7.3	7.1	7.3	7.7	7.8	7.8
Reactor 7	7.9	7.3	7.0	7.5	7.7	7.9	7.9
Reactor 8	7.9	7.1	6.9	7.3	7.6	7.7	7.7

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Reactor 1	7.9	7.5	7.7	7.7	8.1	8.1	8.3
Reactor 2	7.9	8.0	8.1	8.2	8.3	8.3	8.5
Reactor 3	7.9	7.9	8.1	8.2	8.3	8.3	8.5
Reactor 4	7.9	7.9	8.1	8.3	8.3	8.3	8.5
Reactor 5	7.9	7.9	8.0	8.1	8.2	8.2	8.5
Reactor 6	7.9	8.0	8.2	8.3	8.3	8.4	8.6
Reactor 7	7.9	8.2	8.2	8.3	8.4	8.4	8.6
Reactor 8	7.9	7.9	8.0	8.1	8.3	8.2	8.5

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Reactor 1	7.9	7.4	7.6	8.1	8.0	7.3
Reactor 2	7.9	8.3	7.8	8.3	8.4	N
Reactor 3	7.9	8.2	8.1	8.3	7.7	7.9
Reactor 4	7.9	8.2	8.1	8.3	8.3	8.0
Reactor 5	7.9	8.2	8.1	8.3	8.3	8.2
Reactor 6	7.9	8.4	8.4	8.5	7.7	N
Reactor 7	7.9	8.4	8.3	8.4	7.7	7.9
Reactor 8	7.9	8.2	8.2	8.3	8.3	N

Cells with an N indicate that not enough water was available for analysis.

H_2S (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Reactor 1	<0.1	0.80	0.63	N	N	N	6.16
Reactor 2	<0.1	0.37	0.57	N	N	N	4.64
Reactor 3	<0.1	0.35	0.70	N	N	N	7.28
Reactor 4	<0.1	0.40	0.71	N	N	N	7.36
Reactor 5	<0.1	0.56	1.53	N	N	N	6.46
Reactor 6	<0.1	0.41	0.71	N	N	N	4.08
Reactor 7	<0.1	0.47	0.56	N	N	N	8.24
Reactor 8	<0.1	0.52	0.58	N	N	N	5.44

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Reactor 1	<0.1	3.07	2.00	0.48	3.12	3.84	3.36
Reactor 2	<0.1	4.51	1.36	2.40	2.96	2.56	3.12
Reactor 3	<0.1	4.19	2.48	3.76	2.72	4.56	5.60
Reactor 4	<0.1	2.59	5.76	1.60	4.24	6.64	8.64
Reactor 5	<0.1	3.39	1.60	1.60	1.76	4.08	4.16
Reactor 6	<0.1	4.32	3.84	2.56	2.80	3.76	4.64
Reactor 7	<0.1	3.20	3.20	<0.1	1.36	3.20	4.40
Reactor 8	<0.1	N	2.64	N	1.52	4.72	6.16

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Reactor 1	<0.1	3.84	2.40	2.40	8.24	N
Reactor 2	<0.1	2.24	1.52	3.04	5.92	N
Reactor 3	<0.1	3.12	5.20	3.76	N	N
Reactor 4	<0.1	4.16	1.12	4.16	9.76	N
Reactor 5	<0.1	3.76	2.16	2.56	2.40	N
Reactor 6	<0.1	4.16	0.24	5.60	6.40	N
Reactor 7	<0.1	2.96	1.60	4.64	2.72	N
Reactor 8	<0.1	5.44	0.16	1.92	5.36	N

Chloride (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	16.77	16.77	1.69	16.83	16.02	17.78	12.22
Reactor 1	16.77	29.88	2.51	27.17	18.33	20.87	10.31
Reactor 2	16.77	13.65	2.24	16.22	18.14	16.44	9.87
Reactor 3	16.77	16.56	2.56	17.79	21.62	15.95	10.06
Reactor 4	16.77	21.83	1.60	16.95	17.00	16.57	9.35
Reactor 5	16.77	37.93	2.30	17.88	16.56	15.95	8.86
Reactor 6	16.77	19.23	1.65	16.24	15.75	16.25	9.67
Reactor 7	16.77	25.13	2.14	19.62	16.27	15.89	9.93
Reactor 8	16.77	18.45	3.18	15.87	16.27	17.20	10.00

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Initial	16.77	12.01	12.6	13.07	12.11	12.08	13.47
Reactor 1	16.77	11.51	12.06	12.24	11.89	13.56	16.07
Reactor 2	16.77	9.92	10.65	12.84	23.96	10.81	12.78
Reactor 3	16.77	10.47	11.44	12.58	11.39	10.91	12.72
Reactor 4	16.77	10.33	10.79	12.00	11.64	10.54	13.54
Reactor 5	16.77	10.19	11.08	11.47	10.41	10.69	9.59
Reactor 6	16.77	9.19	11.06	11.08	10.65	11.27	17.69
Reactor 7	16.77	16.82	10.95	10.75	11.40	9.20	13.64
Reactor 8	16.77	10.77	11.00	11.42	11.02	11.22	10.82

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Initial	16.77	12.55	13.14	12.91	25.94	12.89
Reactor 1	16.77	67.32	110.95	38.19	24.81	198.06
Reactor 2	16.77	8.32	25.07	16.56	19.25	N
Reactor 3	16.77	8.16	11.67	15.05	0.03	17.60
Reactor 4	16.77	9.36	12.23	15.36	15.28	17.03
Reactor 5	16.77	8.84	12.76	15.07	18.09	13.87
Reactor 6	16.77	102.72	10.17	21.34	16.23	N
Reactor 7	16.77	7.73	14.90	21.40	16.31	18.13
Reactor 8	16.77	8.82	11.56	14.77	13.67	N

Cells with an N indicate that not enough water was available for analysis.

Barium (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Reactor 1	<0.025	0.645	0.413	0.263	0.295	0.209	0.342
Reactor 2	<0.025	0.414	0.290	0.234	0.199	0.217	0.189
Reactor 3	<0.025	0.678	0.554	0.224	0.204	0.336	0.208
Reactor 4	<0.025	0.875	0.286	0.316	0.228	0.348	0.211
Reactor 5	<0.025	1.110	0.358	0.187	0.148	0.226	0.271
Reactor 6	<0.025	0.523	0.280	0.183	0.182	0.228	0.271
Reactor 7	<0.025	0.454	0.339	0.199	0.195	0.280	0.299
Reactor 8	<0.025	0.549	0.334	0.175	0.155	0.212	0.263

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Initial	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Reactor 1	<0.025	0.285	0.254	0.261	0.212	0.203	0.180
Reactor 2	<0.025	0.177	0.162	0.148	0.143	0.115	0.109
Reactor 3	<0.025	0.208	0.190	0.177	0.144	0.144	0.127
Reactor 4	<0.025	0.206	0.184	0.171	0.152	0.148	0.131
Reactor 5	<0.025	0.327	0.385	0.404	0.325	0.222	0.192
Reactor 6	<0.025	0.252	0.193	0.183	0.171	0.139	0.129
Reactor 7	<0.025	0.205	0.190	0.174	0.162	0.137	0.124
Reactor 8	<0.025	0.309	0.361	0.326	0.171	0.172	0.157

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Initial	<0.025	<0.025	N	<0.025	<0.025	<0.025
Reactor 1	<0.025	0.171	0.154	0.135	0.129	0.084
Reactor 2	<0.025	0.095	0.100	0.092	0.098	N
Reactor 3	<0.025	0.114	0.112	0.102	0.089	0.085
Reactor 4	<0.025	0.127	0.109	0.095	0.095	0.105
Reactor 5	<0.025	0.193	0.174	0.144	0.120	0.097
Reactor 6	<0.025	0.113	0.099	0.110	0.100	N
Reactor 7	<0.025	0.107	0.110	0.107	0.105	0.102
Reactor 8	<0.025	0.135	0.127	0.118	0.116	N

Eh (mV)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Reactor 1	278.7	-139.1	-212.0	-120.0	-123.8	-73.2	-105.7
Reactor 2	278.7	-119.1	-179.3	-130.3	-101.3	-108.9	-186.1
Reactor 3	278.7	-151.0	-185.0	-119.2	-149.2	-115.5	-200.6
Reactor 4	278.7	-176.1	-171.7	-171.1	-139.7	-137.9	-203.3
Reactor 5	278.7	-225.4	-194.8	-160.7	-157.7	-160.5	-194.3
Reactor 6	278.7	-235.5	-189.4	-75.2	-132.6	-159.7	-187.5
Reactor 7	278.7	-258.5	-60.6	-182.6	-151.9	-170.7	-173.7
Reactor 8	278.7	-283.9	-158.9	-63.4	-145.2	-150.9	-163.3

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Reactor 1	278.7	-216.7	-268.3	-290.9	-229.4	-238.8	-273.2
Reactor 2	278.7	-229.0	-283.8	-290.5	-245.6	-225.5	-261.1
Reactor 3	278.7	-217.2	-303.6	-295.2	-231.7	-228.2	-254.4
Reactor 4	278.7	-257.4	-299.6	-312.6	-248.5	-254.6	-277.9
Reactor 5	278.7	-233.8	-249.4	-261.8	-201.7	-234.2	-266.4
Reactor 6	278.7	-231.7	-294.0	-300.2	-262.1	-237.5	-262.2
Reactor 7	278.7	-245.5	-273.0	-278.9	-243.1	-226.4	-250.6
Reactor 8	278.7	-216.0	-239.2	-248.6	-237.2	-236.0	-245.8

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Reactor 1	278.7	-298.5	-287.6	-246.5	-259.8	-336.7
Reactor 2	278.7	-285.2	-280.7	-231.1	-288.5	N
Reactor 3	278.7	-293.1	-304.1	-241.4	-294.5	-351.1
Reactor 4	278.7	-298.2	-292.5	-247.5	-287.0	-354.4
Reactor 5	278.7	-271.5	-263.5	-220.7	-264.1	-287.2
Reactor 6	278.7	-276.4	-276.2	-181.1	-297.3	N
Reactor 7	278.7	-280.7	-265.9	-210.8	-279.7	-330.3
Reactor 8	278.7	-280.5	-283.5	-215.3	-264.4	N

Cells with an N indicate that not enough water was available for analysis.

HCO3 (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Reactor 1	148.87	401.83	431.20	1336.41	1089.11	911.75	770.23
Reactor 2	148.87	366.88	372.77	556.02	403.46	453.91	506.61
Reactor 3	148.87	380.69	499.32	670.92	536.86	626.81	578.77
Reactor 4	148.87	406.12	370.52	569.41	477.74	535.64	520.25
Reactor 5	148.87	653.80	595.13	812.35	612.90	644.97	687.42
Reactor 6	148.87	399.63	375.13	515.53	493.71	513.59	459.66
Reactor 7	148.87	485.97	270.15	624.96	556.68	532.42	541.05
Reactor 8	148.87	459.66	374.11	602.11	590.63	607.29	598.50

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Reactor 1	148.87	N	578.37	626.90	503.28	521.01	494.48
Reactor 2	148.87	N	430.81	462.88	482.78	406.97	368.74
Reactor 3	148.87	N	501.50	559.10	472.45	497.90	452.96
Reactor 4	148.87	N	495.64	552.49	N	494.28	459.46
Reactor 5	148.87	N	734.49	831.10	713.84	609.74	497.18
Reactor 6	148.87	N	462.13	538.53	520.25	450.10	411.39
Reactor 7	148.87	N	569.20	572.33	539.21	502.52	467.88
Reactor 8	148.87	N	558.27	568.94	521.71	612.35	538.57

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Reactor 1	148.87	420.03	466.25	428.44	383.23	449.29
Reactor 2	148.87	332.16	388.37	662.24	322.75	N
Reactor 3	148.87	357.08	418.91	376.33	N	398.97
Reactor 4	148.87	385.94	386.60	421.08	408.53	504.64
Reactor 5	148.87	397.06	429.78	365.56	381.42	350.31
Reactor 6	148.87	338.64	366.96	391.57	352.46	N
Reactor 7	148.87	343.80	540.15	402.70	419.01	411.16
Reactor 8	148.87	436.06	427.17	N	382.27	N

Sulphate (mg/L)

Treatment	Initial	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Initial	1592.39	1592.39	1583	1657.84	1603.83	1722.58	1484.93
Reactor 1	1592.39	1017.25	956.80	255.40	200.90	291.85	616.73
Reactor 2	1592.39	1176.21	1010.00	892.02	1088.70	948.94	883.00
Reactor 3	1592.39	948.53	829.60	764.28	945.38	807.15	837.90
Reactor 4	1592.39	1139.50	860.00	847.95	999.39	944.94	812.86
Reactor 5	1592.39	983.17	787.00	442.17	696.12	611.06	592.45
Reactor 6	1592.39	1168.63	1018.10	920.02	1019.83	996.47	846.85
Reactor 7	1592.39	1238.10	1180.80	839.49	929.40	868.97	817.32
Reactor 8	1592.39	1208.26	1041.30	799.92	865.21	881.00	791.11

Treatment	Initial	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Initial	1592.39	1547.33	1541.65	1525.3	1523.8	1523.1	1435.73
Reactor 1	1592.39	941.61	953.30	999.80	1034.53	1014.66	972.71
Reactor 2	1592.39	709.00	1010.94	1007.36	1015.36	865.80	932.01
Reactor 3	1592.39	905.08	1011.05	994.23	1010.27	938.11	948.51
Reactor 4	1592.39	879.49	923.88	928.53	905.65	968.72	1006.37
Reactor 5	1592.39	513.42	589.34	928.60	919.42	846.73	939.45
Reactor 6	1592.39	755.32	933.09	632.29	695.39	883.75	928.53
Reactor 7	1592.39	652.43	867.44	904.73	923.56	824.67	890.66
Reactor 8	1592.39	862.41	901.15	891.78	908.95	847.09	922.34

Treatment	Initial	Week 13	Week 14	Week 15	Week 16	Week 20
Initial	1592.39	1475.48	1483.39	1506.3	1458.75	1503.18
Reactor 1	1592.39	1060.91	1091.92	1144.83	1130.62	1092.20
Reactor 2	1592.39	930.97	993.72	1053.05	1206.90	N
Reactor 3	1592.39	979.53	979.89	1020.19	N	944.19
Reactor 4	1592.39	1053.11	1004.29	1081.68	1089.52	1056.38
Reactor 5	1592.39	1016.47	1025.18	1072.31	1080.74	917.92
Reactor 6	1592.39	N	844.48	1184.34	1242.03	N
Reactor 7	1592.39	899.05	924.64	1042.10	1157.47	1051.32
Reactor 8	1592.39	937.31	936.83	1053.79	1026.12	N

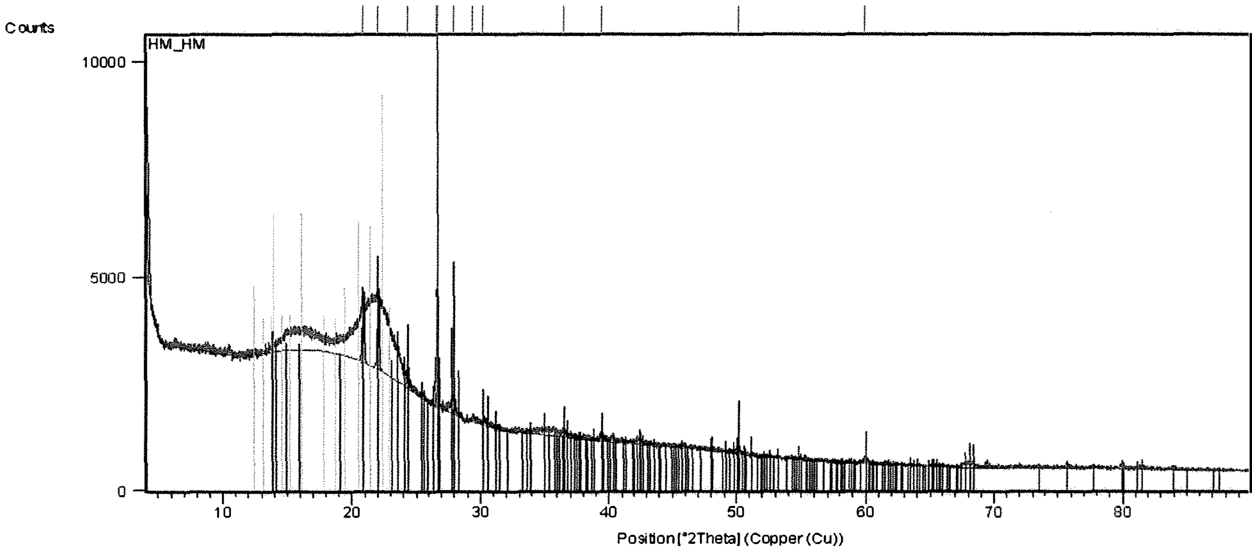
Cells with an N indicate that not enough water was available for analysis.

APPENDIX 5

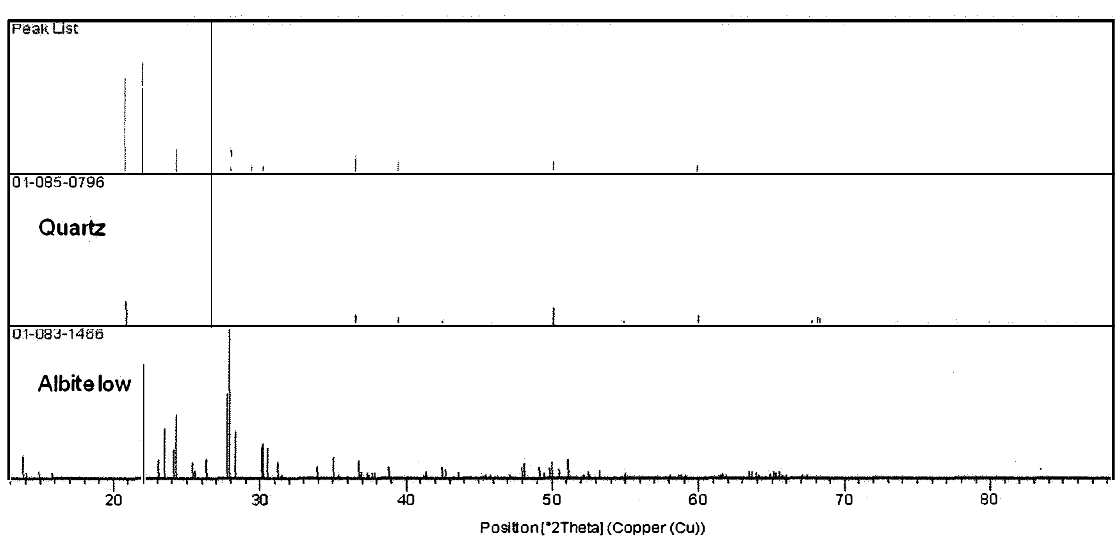
X-RAY DIFFRACTION PATTERNS

Horse Manure

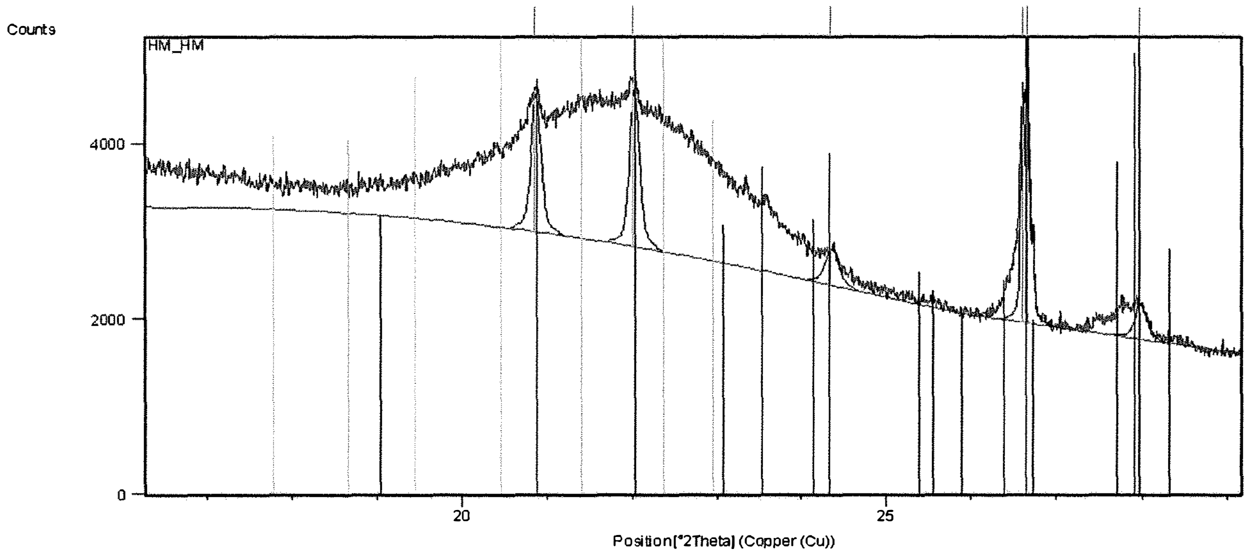
(a) X-ray diffraction pattern for horse manure (5 – 90 °2-theta).



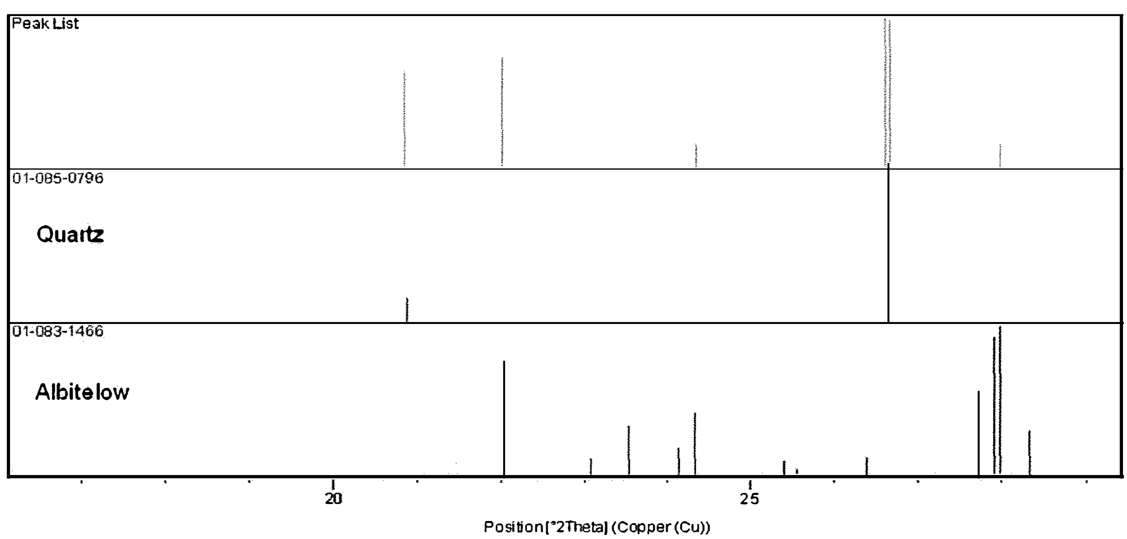
(b) ICDD PDF-2 database peak matches for horse manure.



(c) Expanded view 16 to 29 ^{o}2-theta, showing key x-ray diffraction peaks for horse manure.

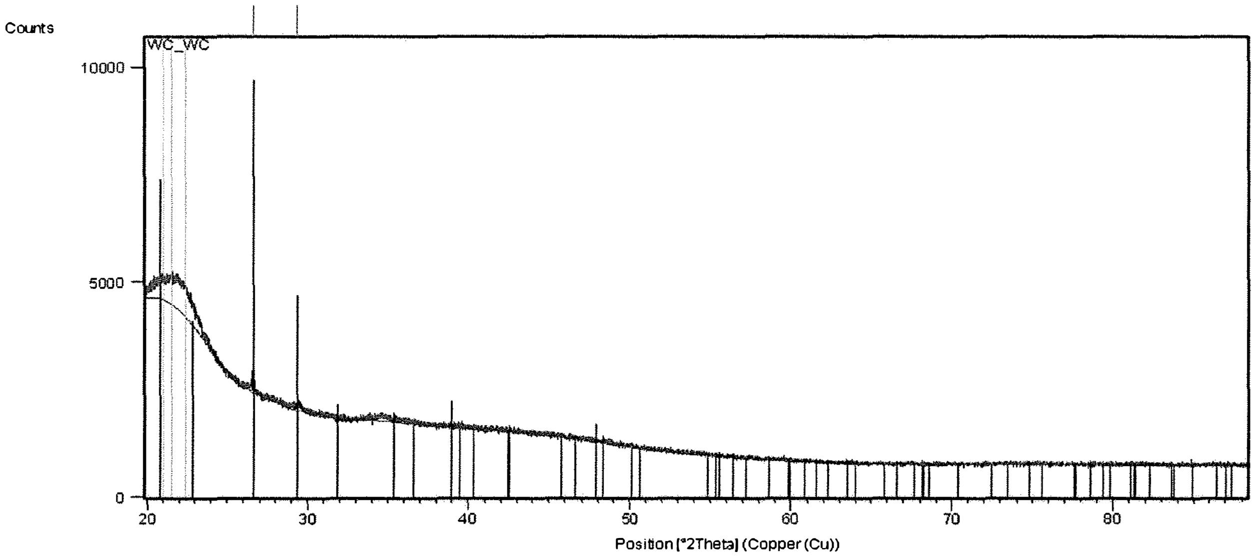


(d) Expanded view 16 to 29 ^{o}2-theta, showing ICDD PDF-2 database peak matches for horse manure.

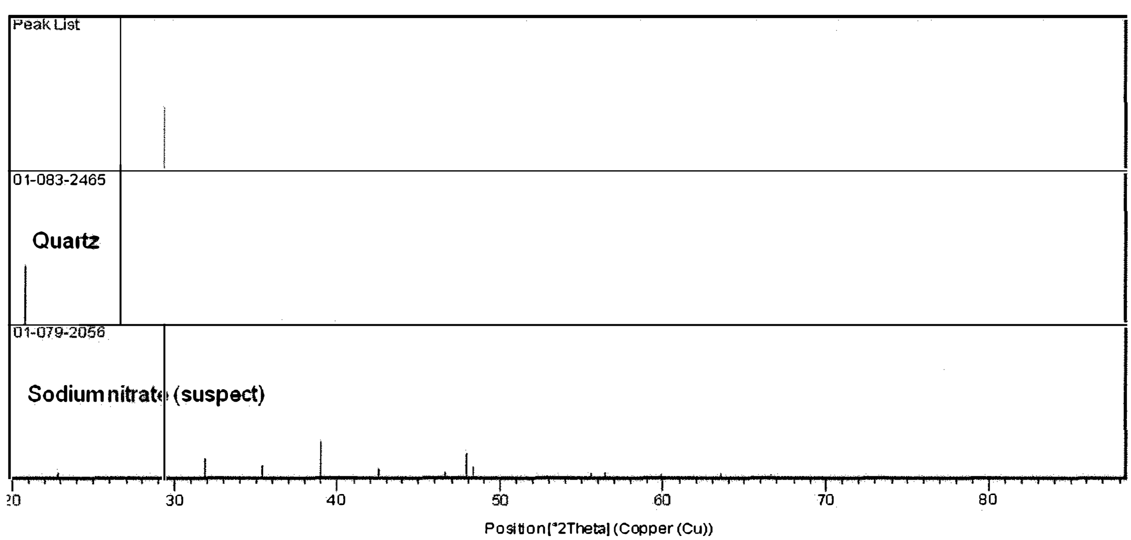


Wood Chips

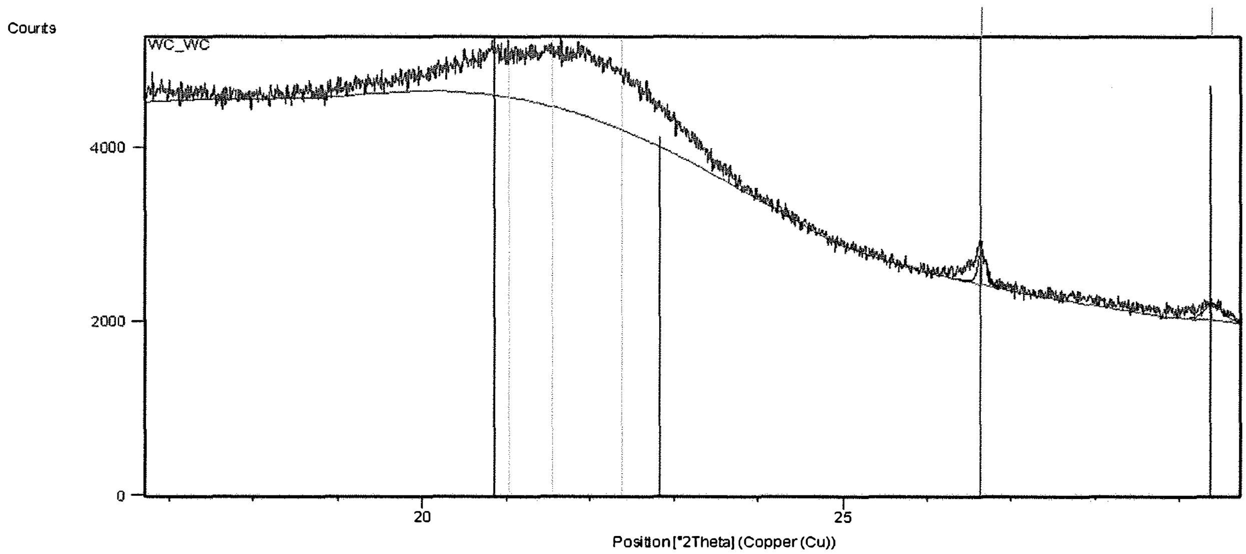
(a) X-ray diffraction pattern for wood chips (20 – 88 ^{o}2-theta).



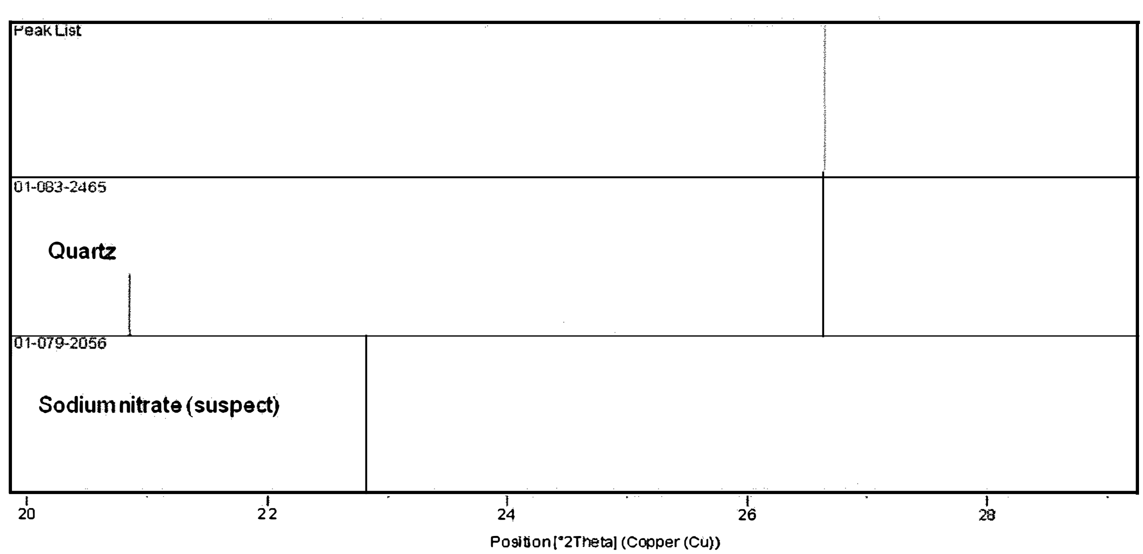
(b) ICDD PDF-2 database peak matches for wood chips.



(c) Expanded view 17 to 30 ^{o}2-theta, showing key x-ray diffraction peaks for wood chips.

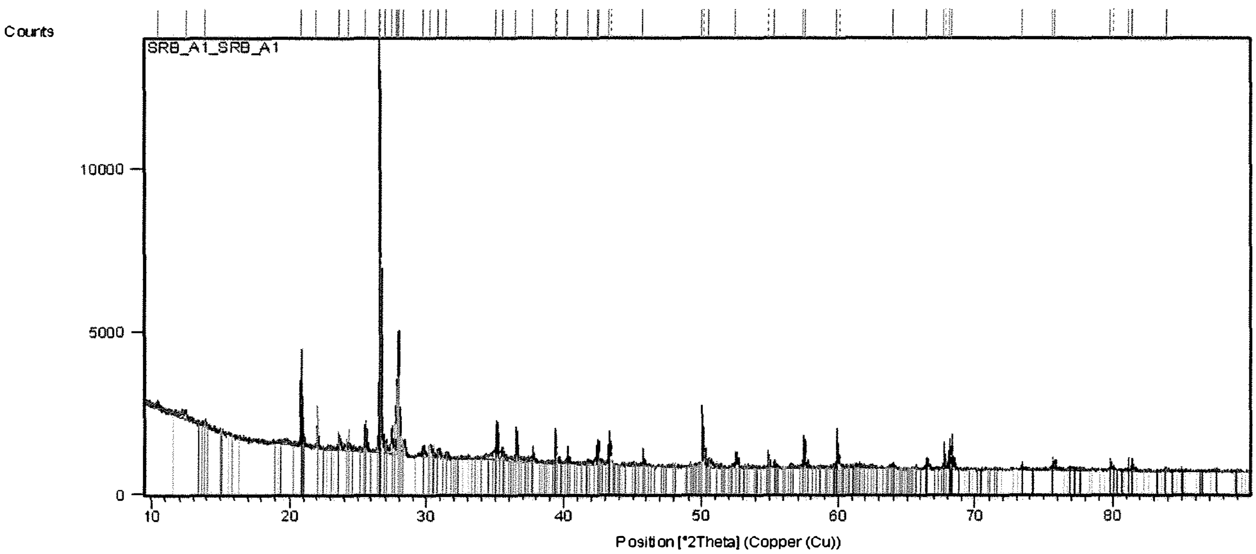


(d) Expanded view 17 to 30 ^{o}2-theta, showing ICDD PDF-2 database peak matches for wood chips.

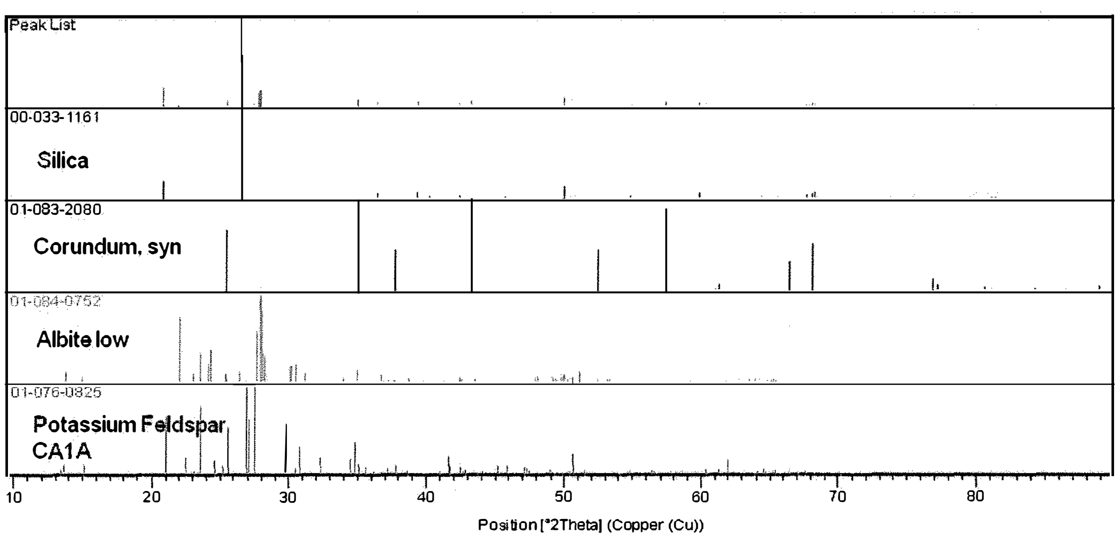


Creek Sediment

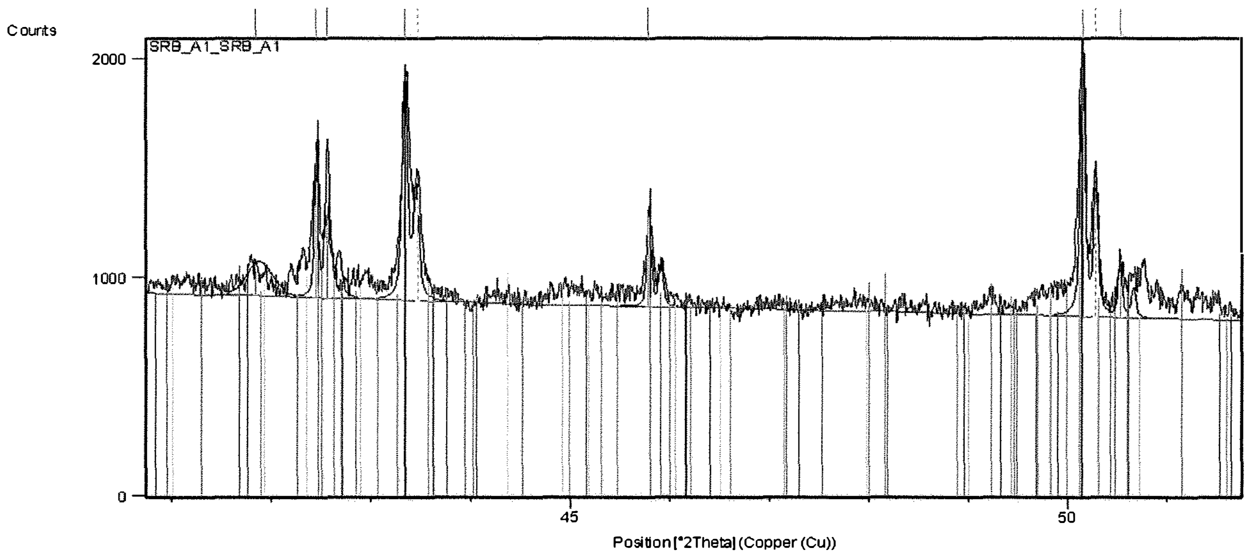
(a) X-ray diffraction pattern for creek sediment (10 – 90 °2-theta).



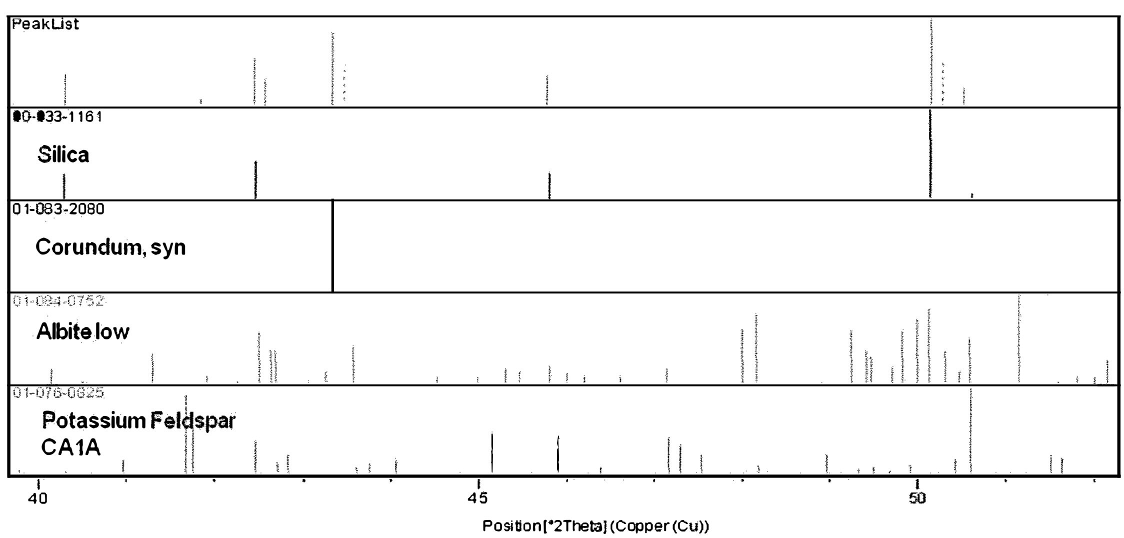
(b) ICDD PDF-2 database peak matches for creek sediment.



(c) Expanded view 40 to 52 °2-theta, showing key x-ray diffraction peaks for creek sediment.

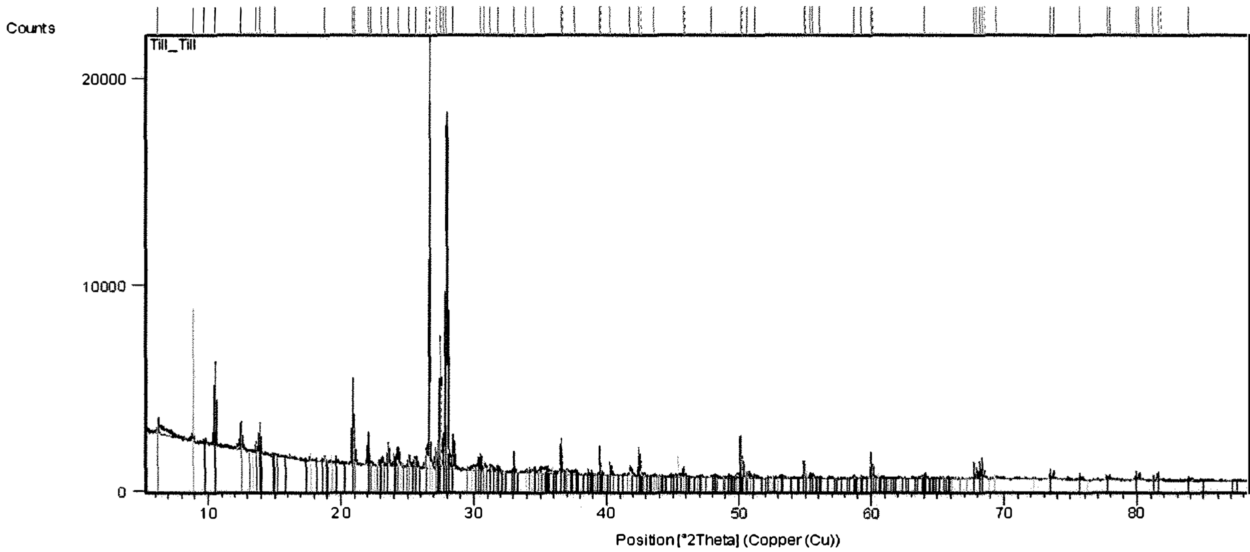


(d) Expanded view 40 to 52 °2-theta, showing ICDD PDF-2 database peak matches for creek sediment.

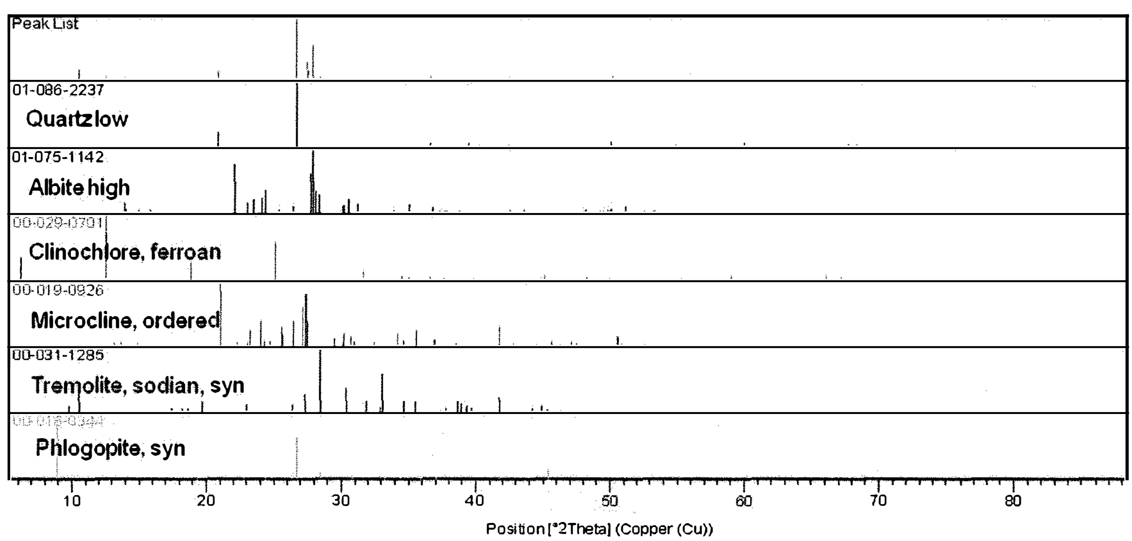


Glacial Till

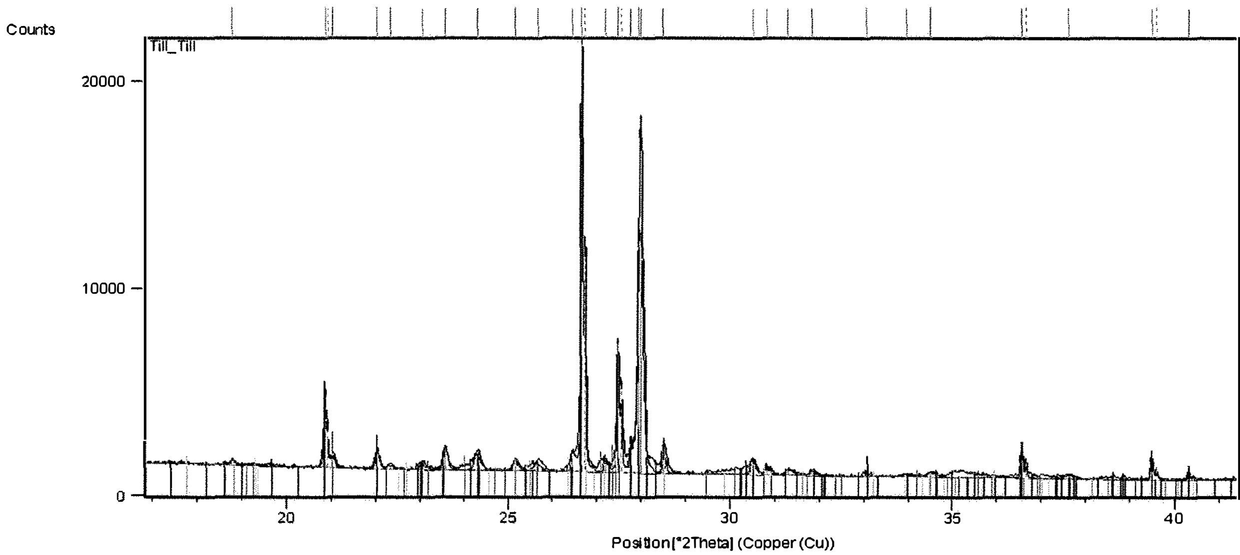
(a) X-ray diffraction pattern for glacial till (5 – 88 ^{o}2-theta).



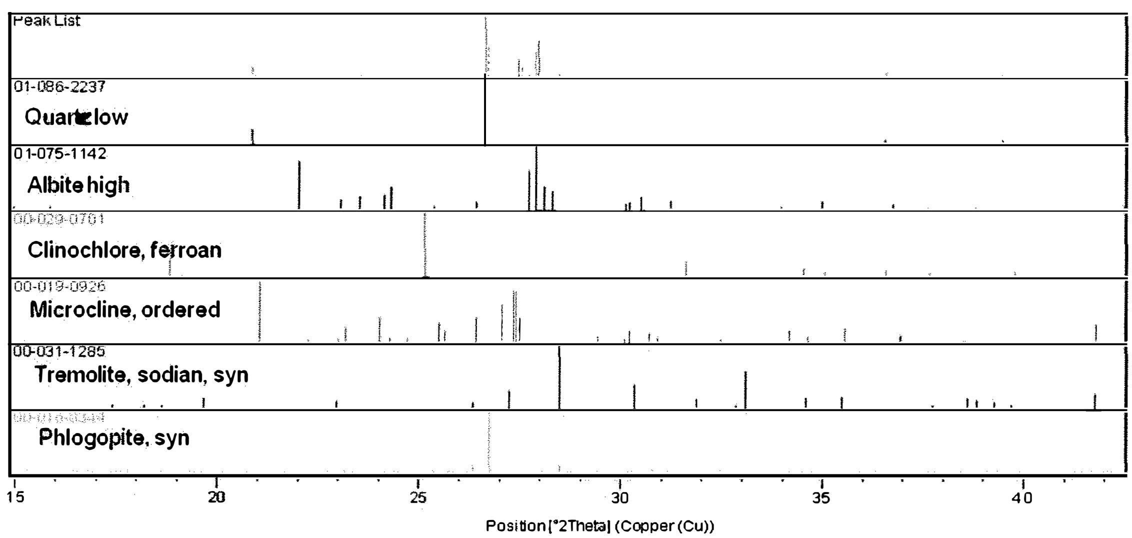
(b) ICDD PDF-2 database peak matches for glacial till.



(c) Expanded view 15 to 42 °2-theta, showing key x-ray diffraction peaks for glacial till.

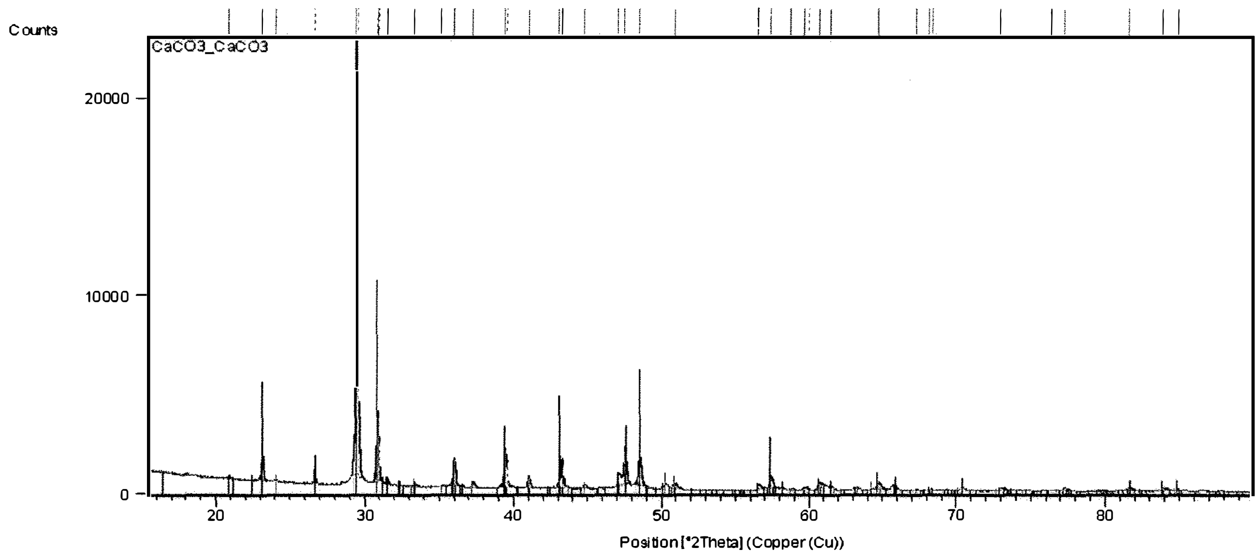


(d) Expanded view 15 to 42 °2-theta, showing ICDD PDF-2 database peak matches for glacial till.

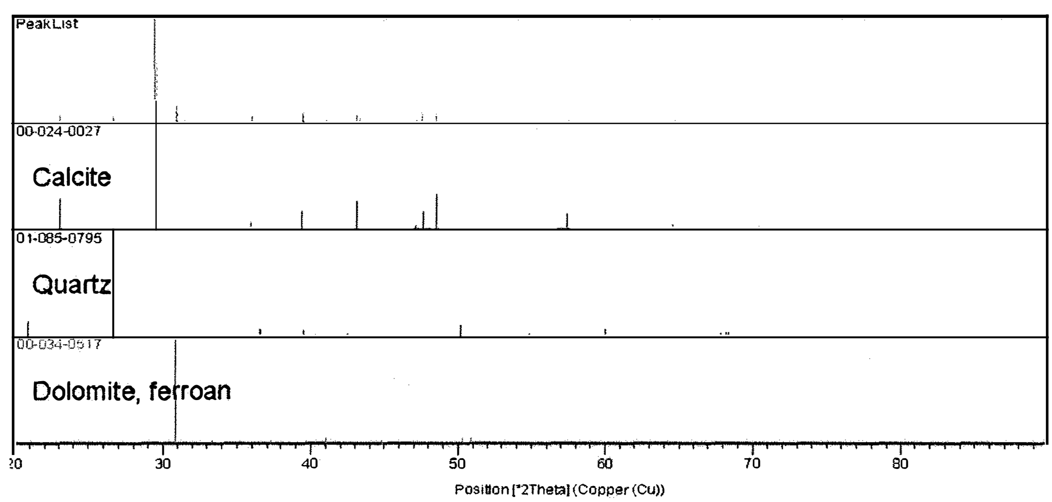


Mosher Carbonate Rock

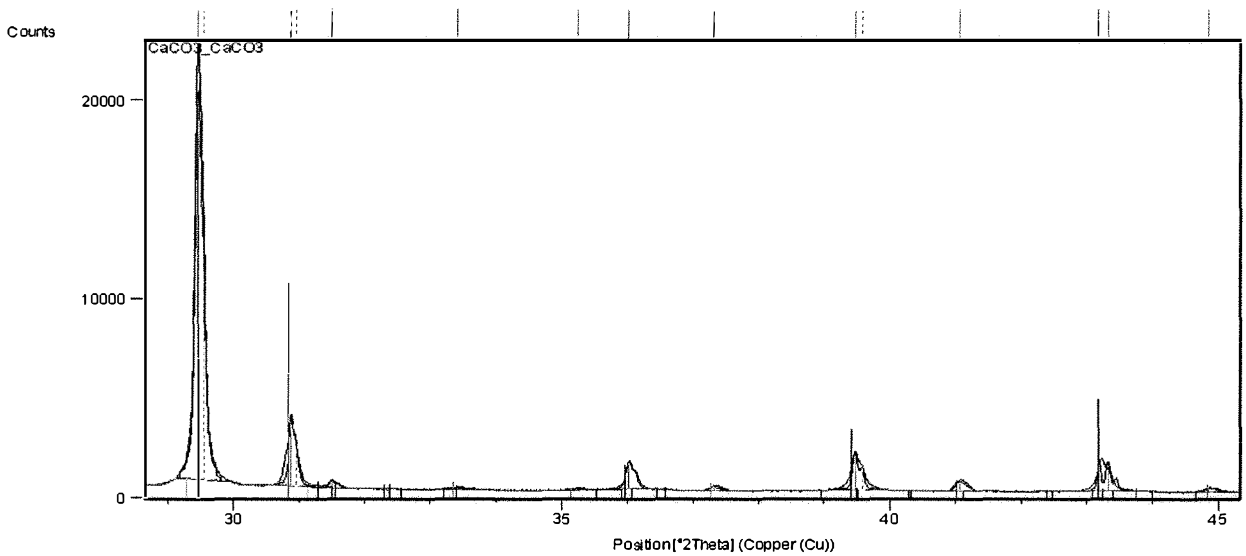
(a) X-ray diffraction pattern for Mosher carbonate rock (16 – 90 °2-theta).



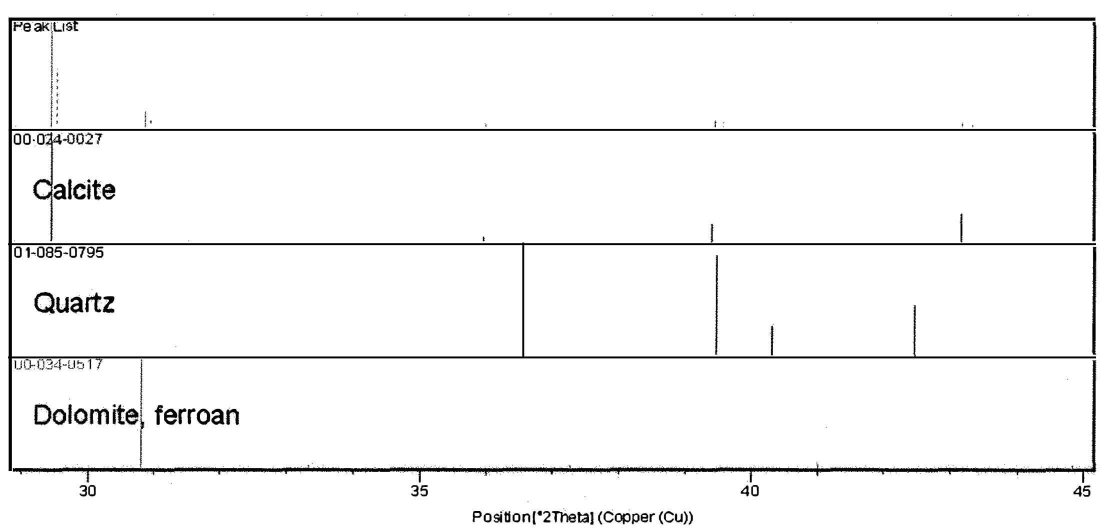
(b) ICDD PDF-2 database peak matches for Mosher carbonate rock.



(c) Expanded view 29 to 45 ^{o}2-theta, showing key x-ray diffraction peaks for Mosher carbonate rock.

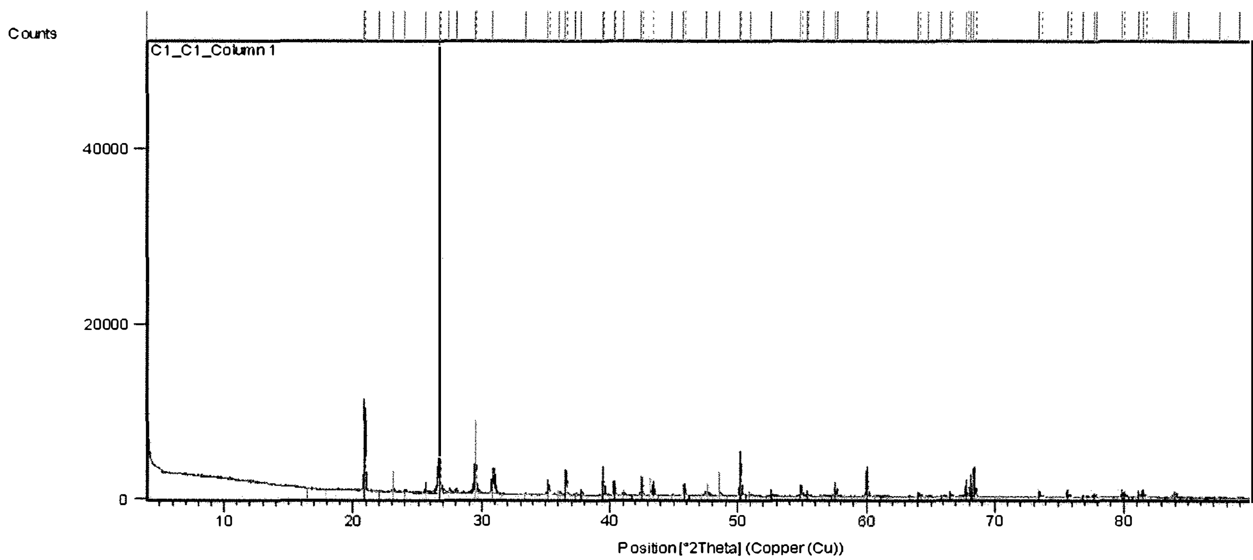


(d) Expanded view 29 to 45 ^{o}2-theta, showing ICDD PDF-2 database peak matches for glacial till.

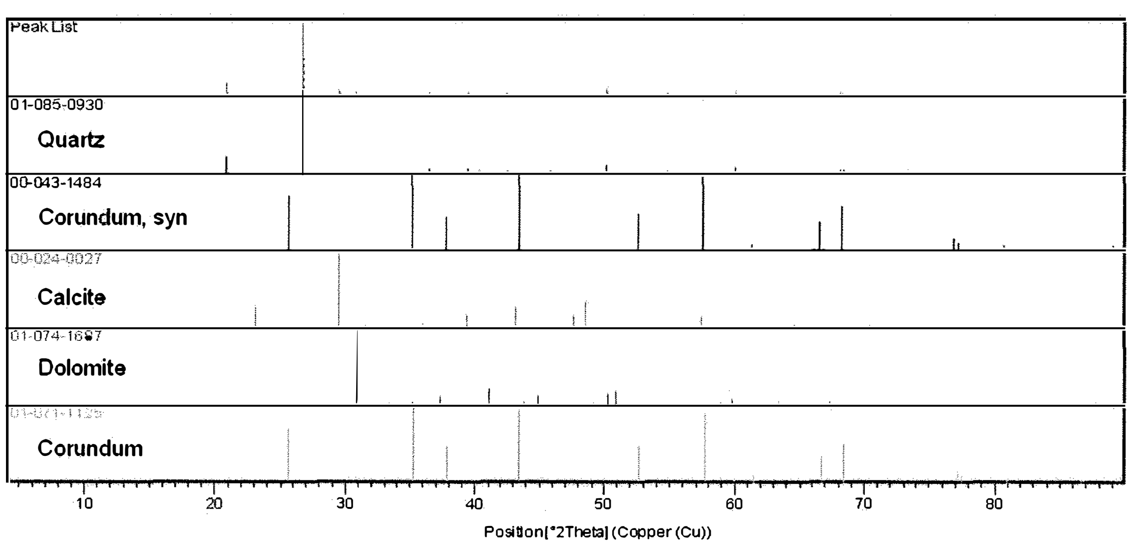


Flow-through Reactor 1

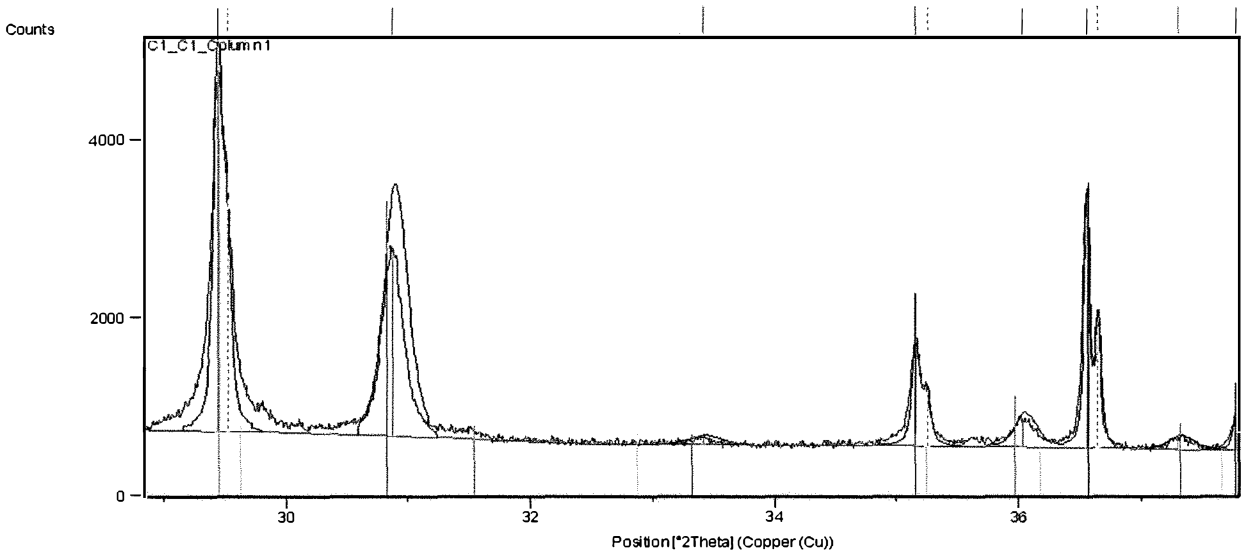
(a) X-ray diffraction pattern for flow-through reactor 1 (5 – 90 ^{o}2-theta).



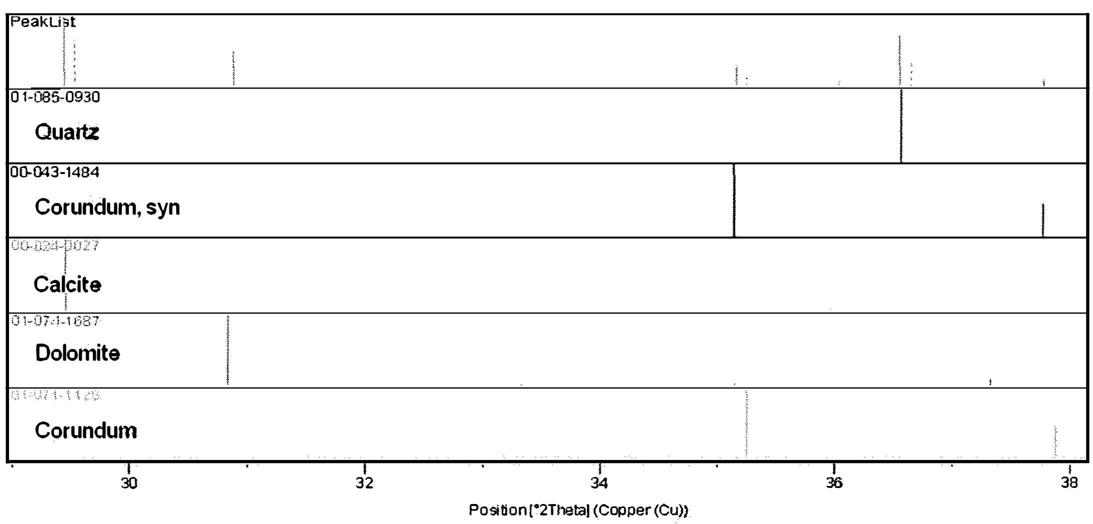
(b) ICDD PDF-2 database peak matches for flow-through reactor 1.



(c) Expanded view 29 to 38 ^{o}2-theta, showing key x-ray diffraction peaks for reactor 1.

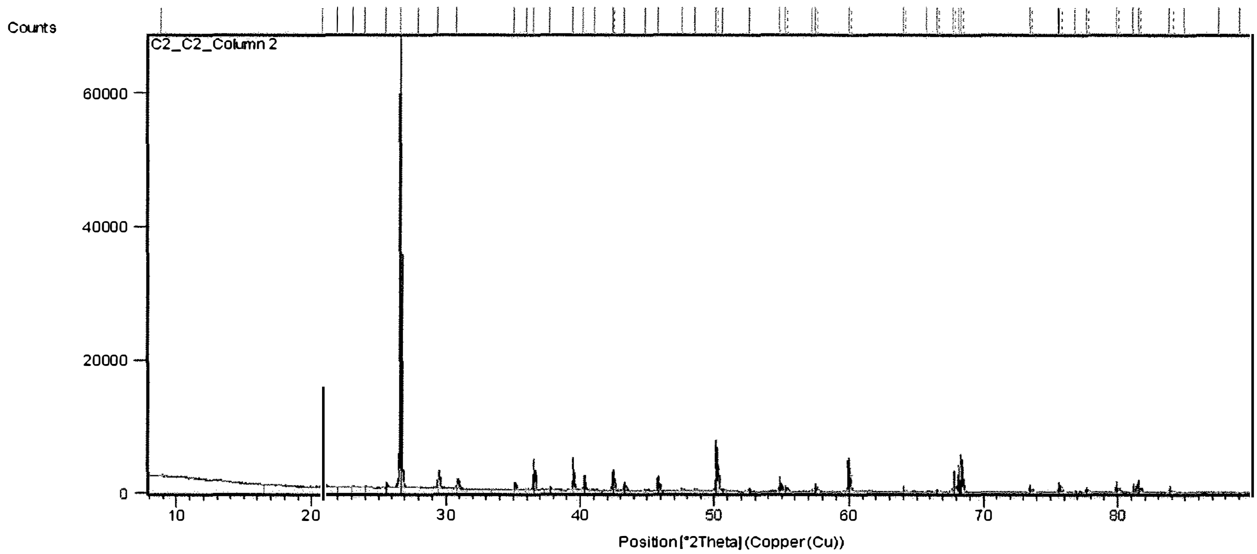


(d) Expanded view 29 to 38 ^{o}2-theta, showing ICDD PDF-2 database peak matches for reactor 1.

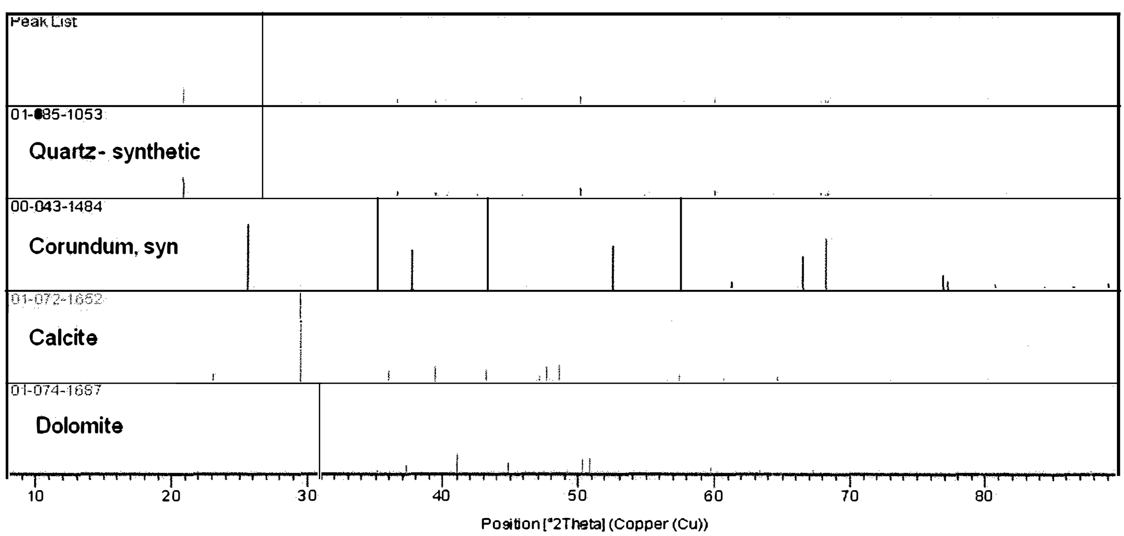


Flow-through Reactor 2

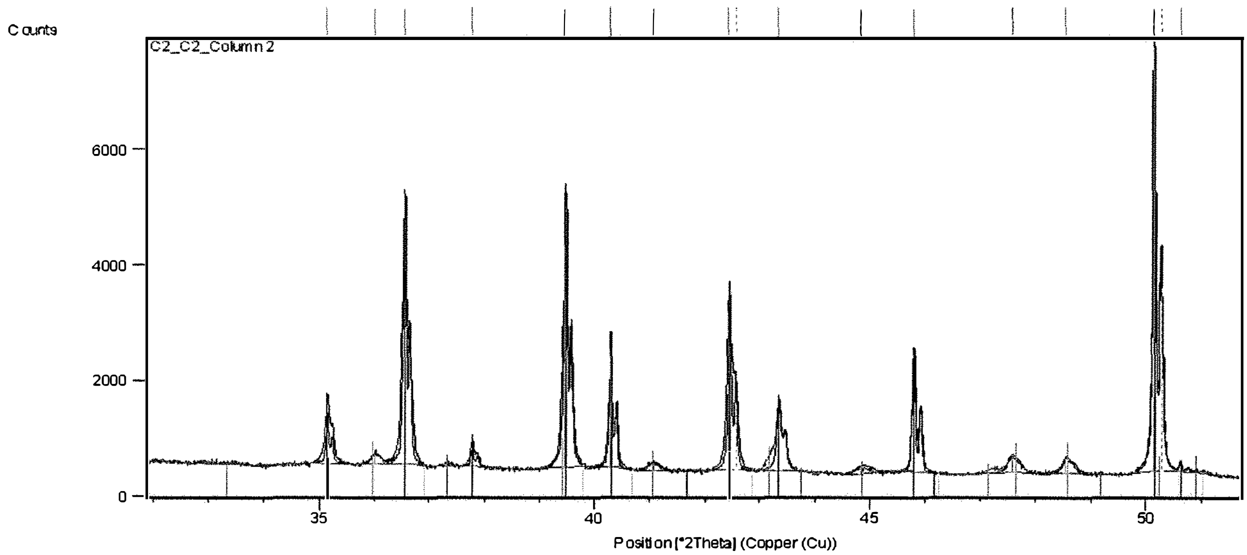
(a) X-ray diffraction pattern for flow-through reactor 2 (8 – 90 ^{o}2-theta).



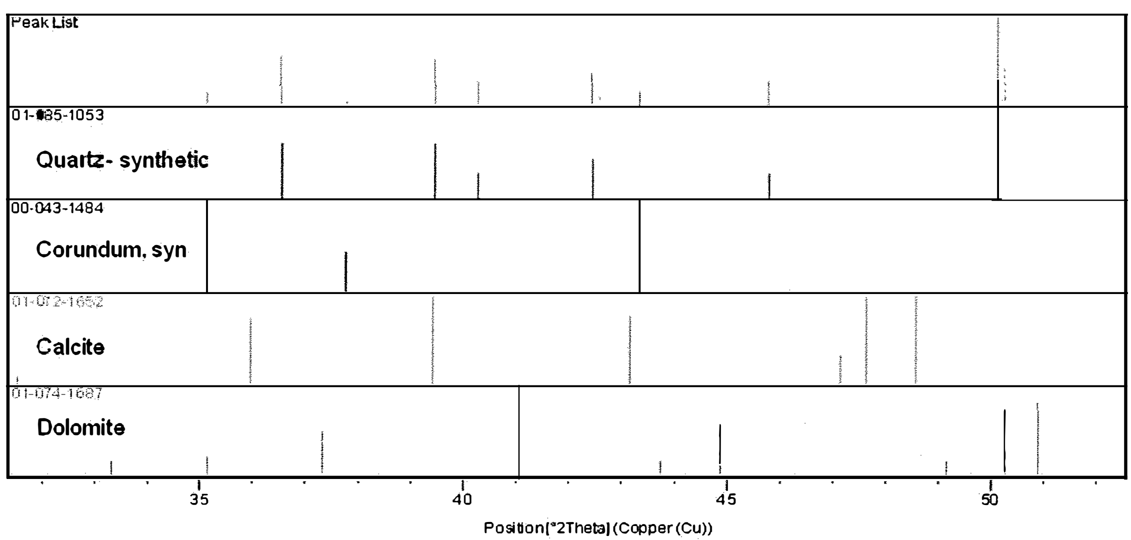
(b) ICDD PDF-2 database peak matches for flow-through reactor 2.



(c) Expanded view 32 to 52 °2-theta, showing key x-ray diffraction peaks for reactor 2.

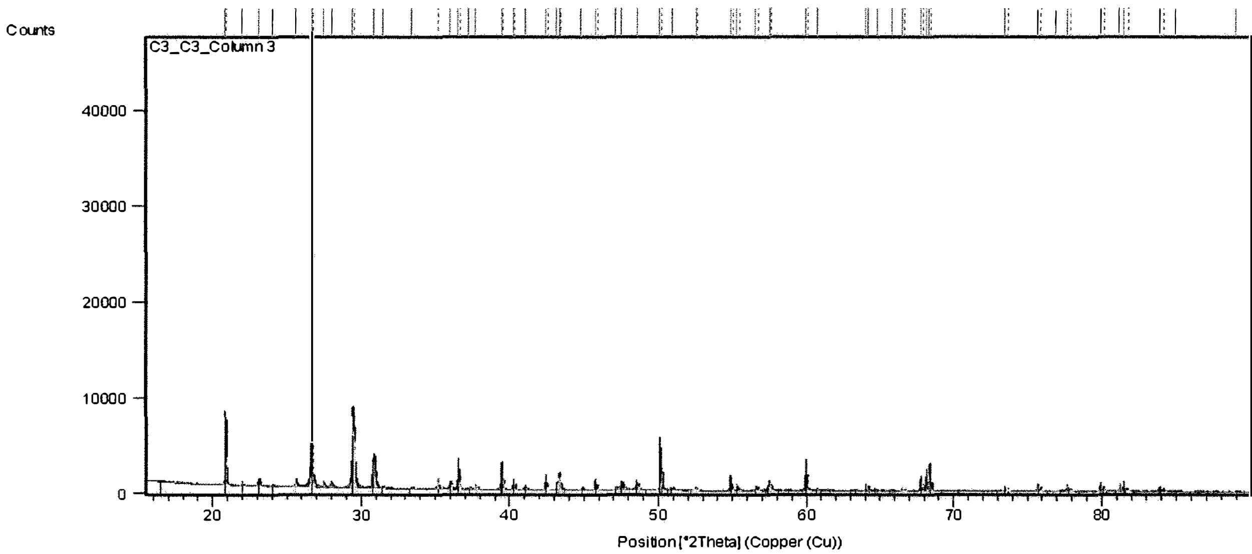


(d) Expanded view 32 to 52 °2-theta, showing ICDD PDF-2 database peak matches for reactor 2.

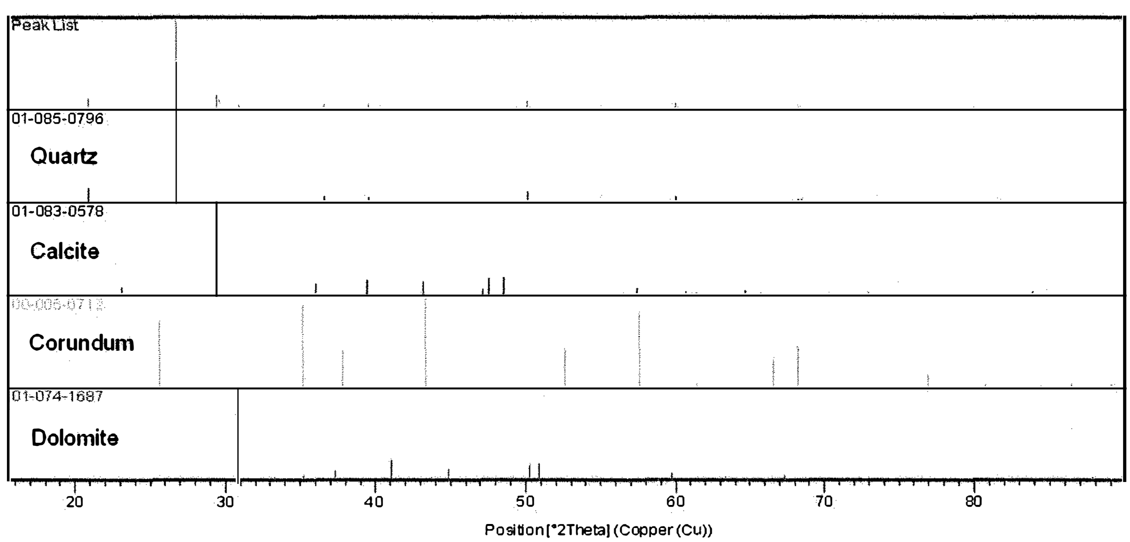


Flow-through Reactor 3

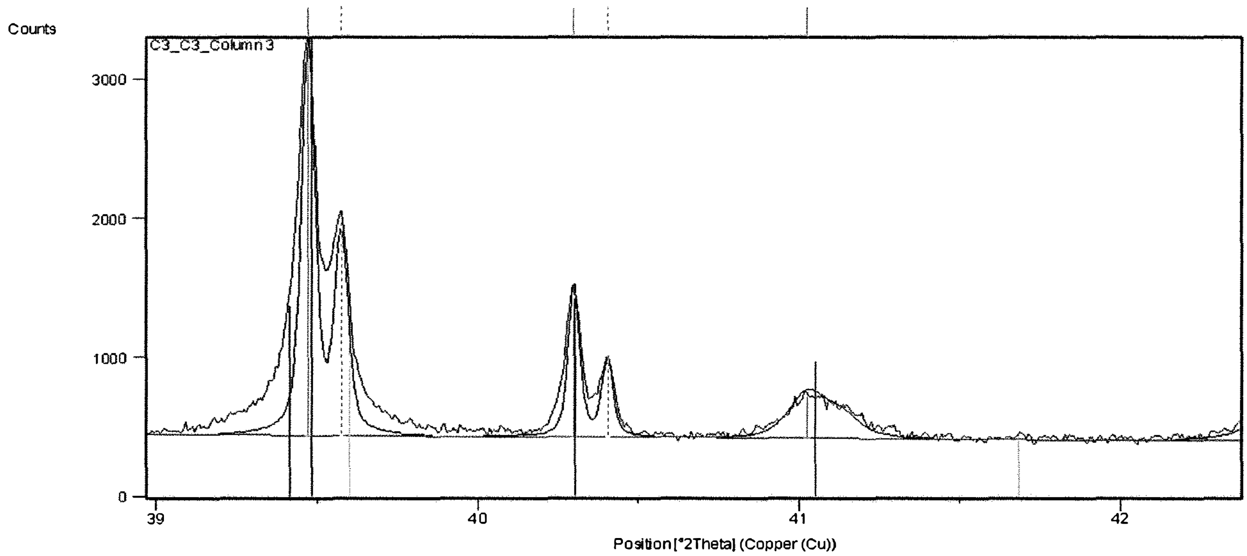
(a) X-ray diffraction pattern for flow-through reactor 3 (16 – 90 ^{o}2-theta).



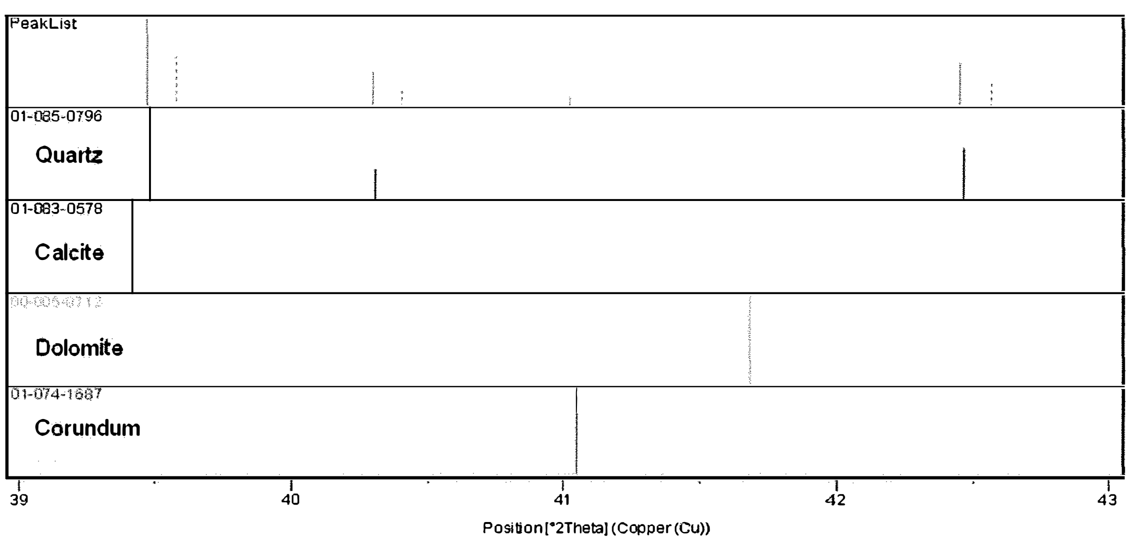
(b) ICDD PDF-2 database peak matches for flow-through reactor 3.



(c) Expanded view 39 to 43 ^{o}2-theta, showing key x-ray diffraction peaks for reactor 3.

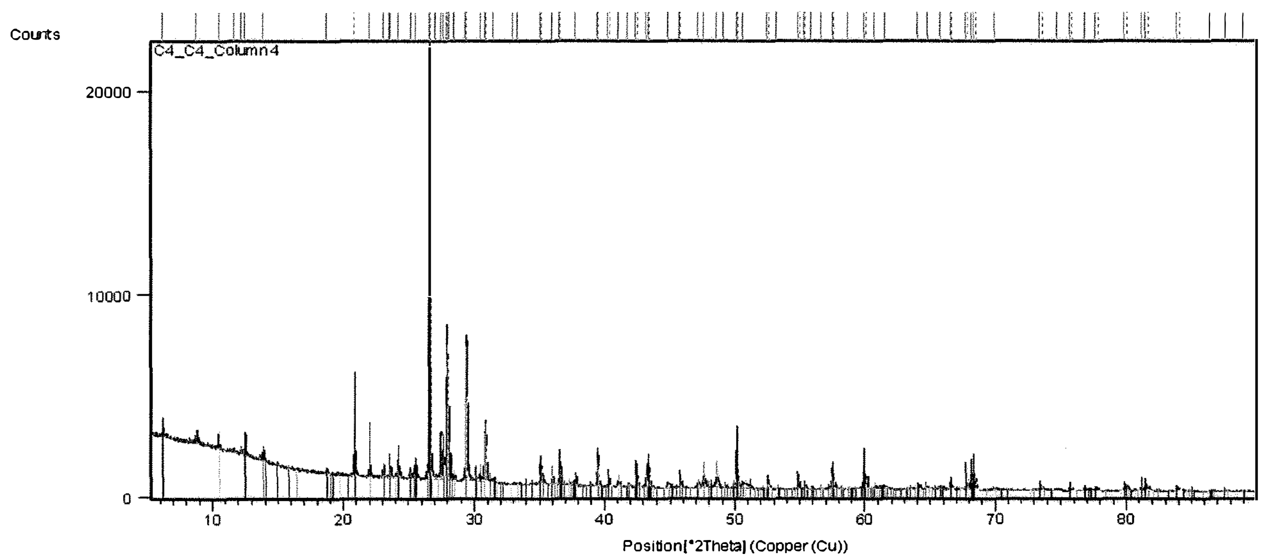


(d) Expanded view 39 to 43 ^{o}2-theta, showing ICDD PDF-2 database peak matches for reactor 3.

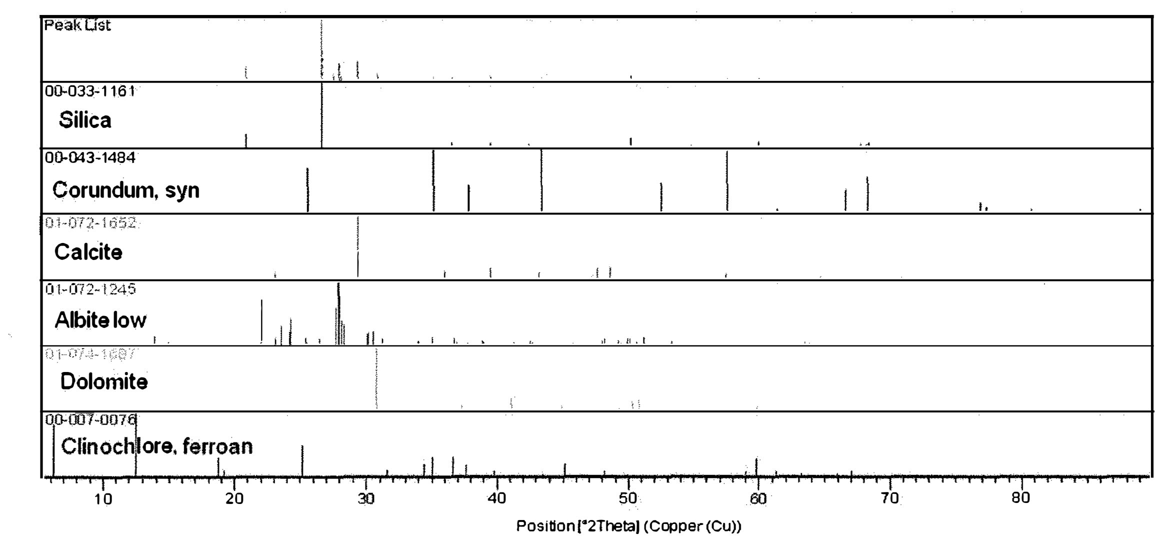


Flow-through Reactor 4

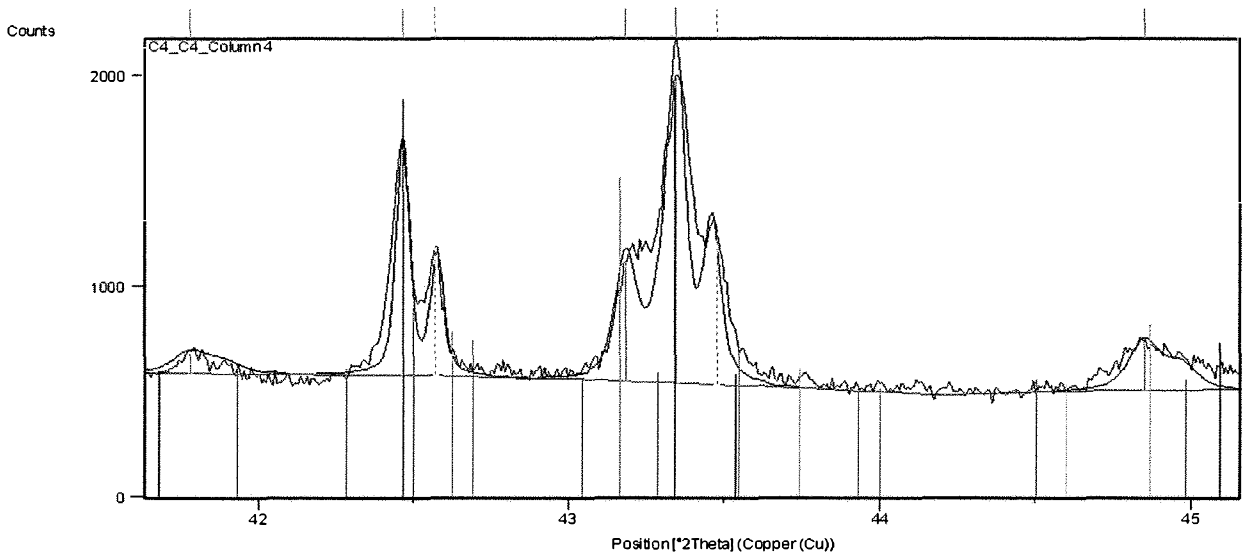
(a) X-ray diffraction pattern for flow-through reactor 4 (5 – 90 ^{o}2-theta).



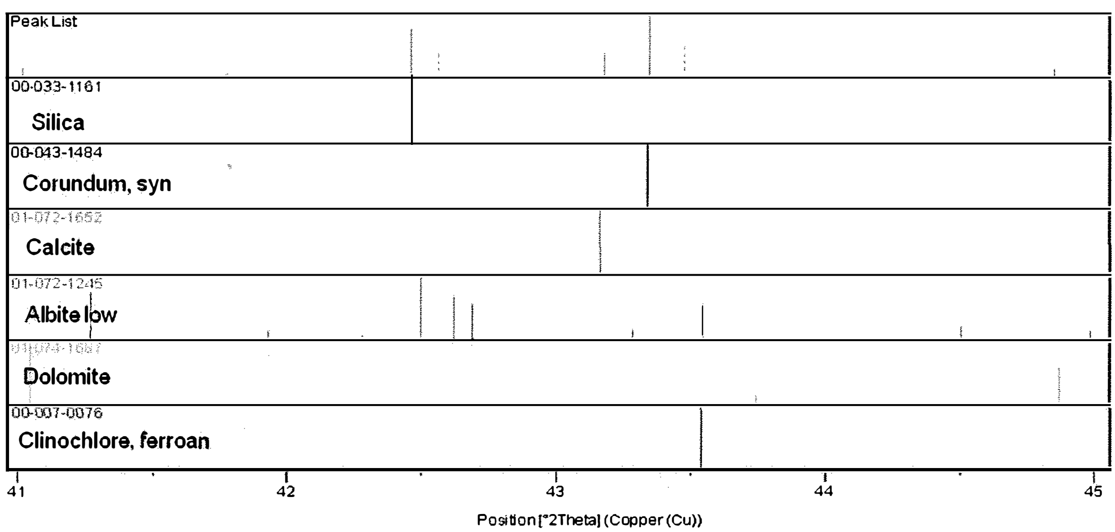
(b) ICDD PDF-2 database peak matches for flow-through reactor 4.



(c) Expanded view 41 to 45 °2-theta, showing key x-ray diffraction peaks for reactor 4.

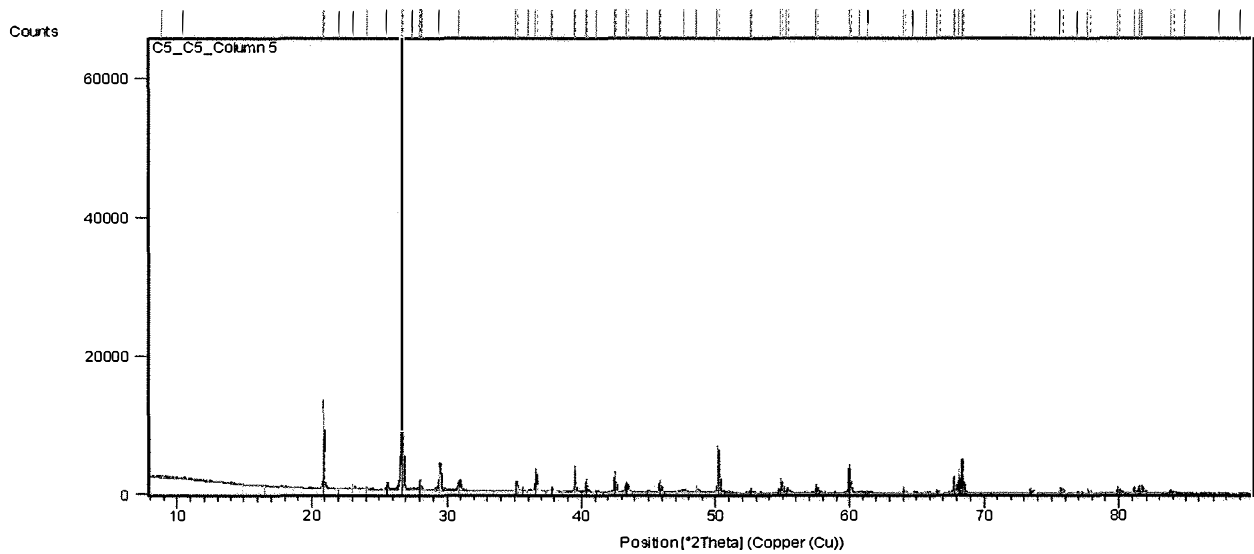


(d) Expanded view 41 to 45 °2-theta, showing ICDD PDF-2 database peak matches for reactor 4.

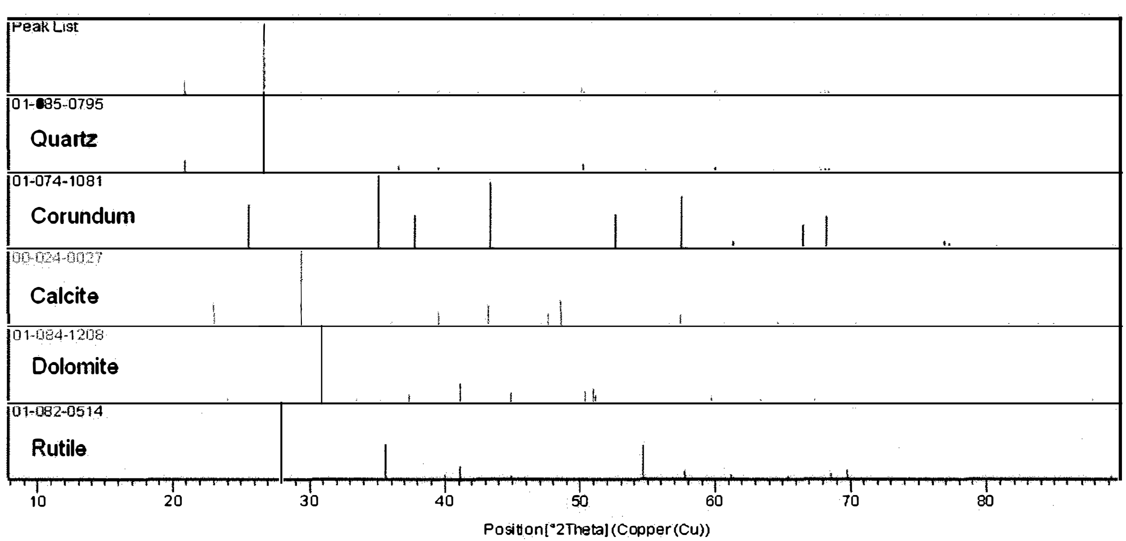


Flow-through Reactor 5

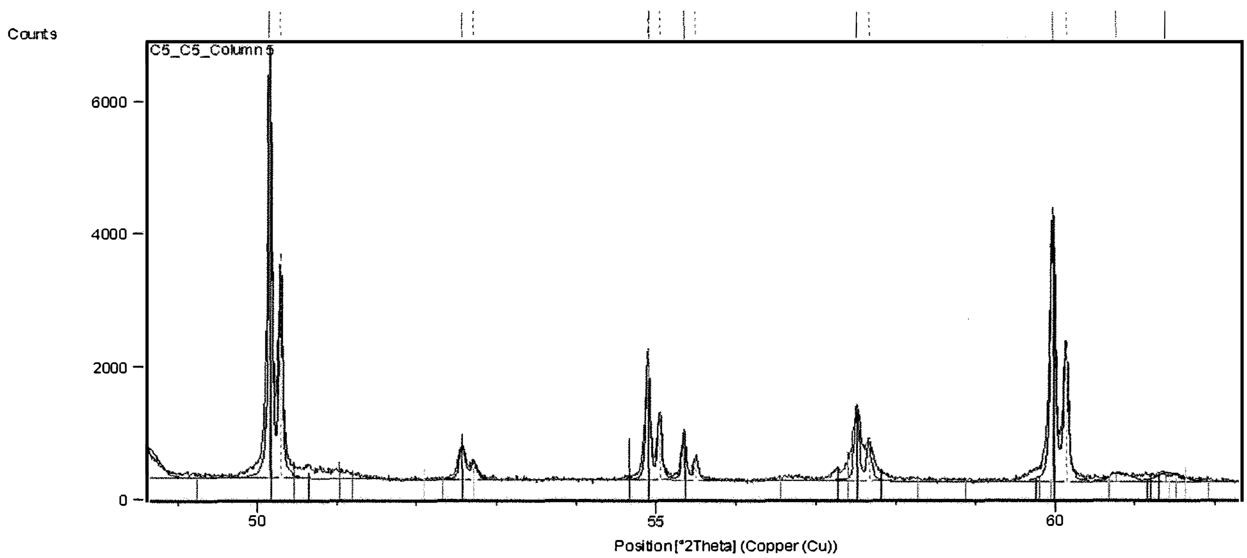
(a) X-ray diffraction pattern for flow-through reactor 5 (8 – 90 ^{o}2-theta).



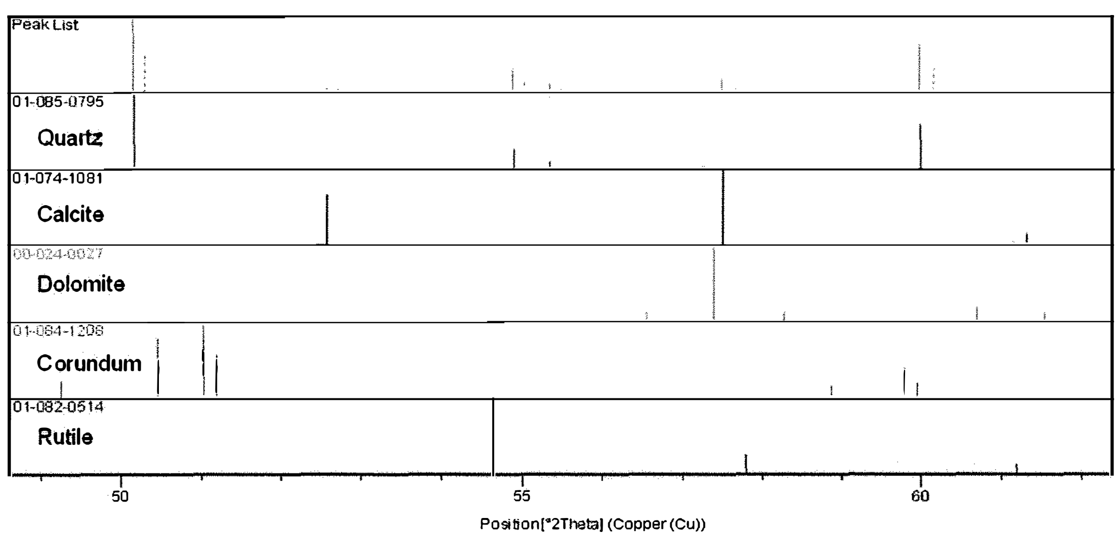
(b) ICDD PDF-2 database peak matches for flow-through reactor 5.



(c) Expanded view 49 to 62 °2-theta, showing key x-ray diffraction peaks for reactor 5.

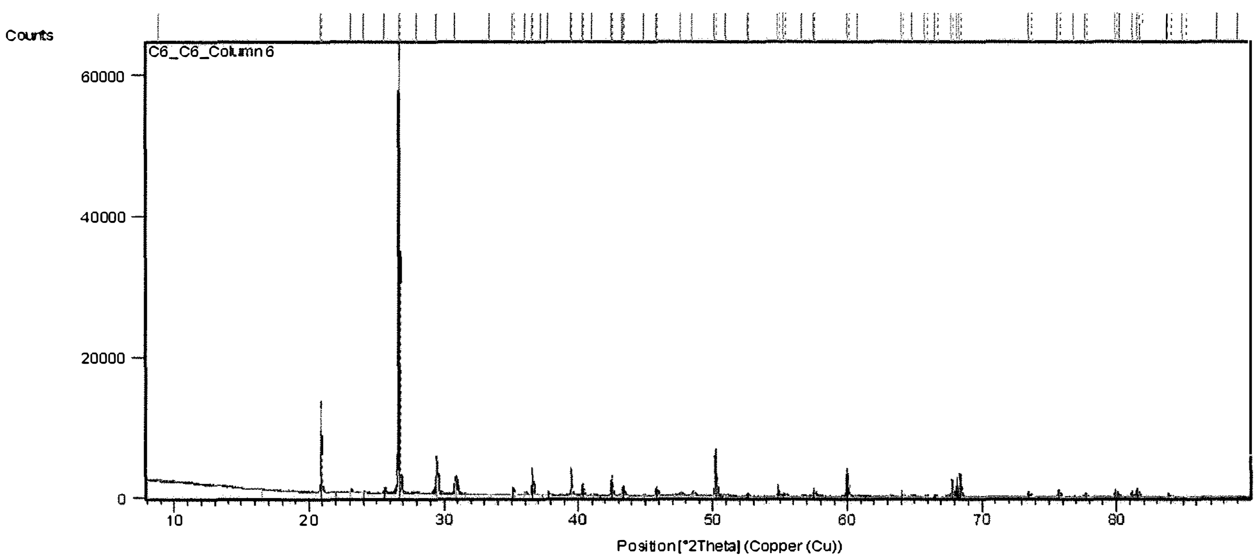


(d) Expanded view 49 to 62 °2-theta, showing ICDD PDF-2 database peak matches for reactor 5.

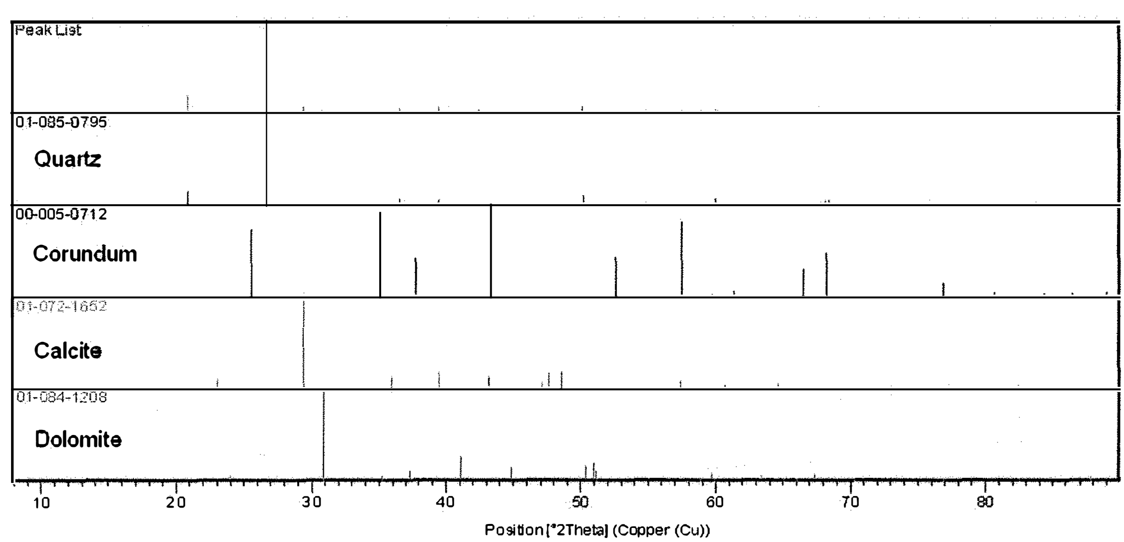


Flow-through Reactor 6

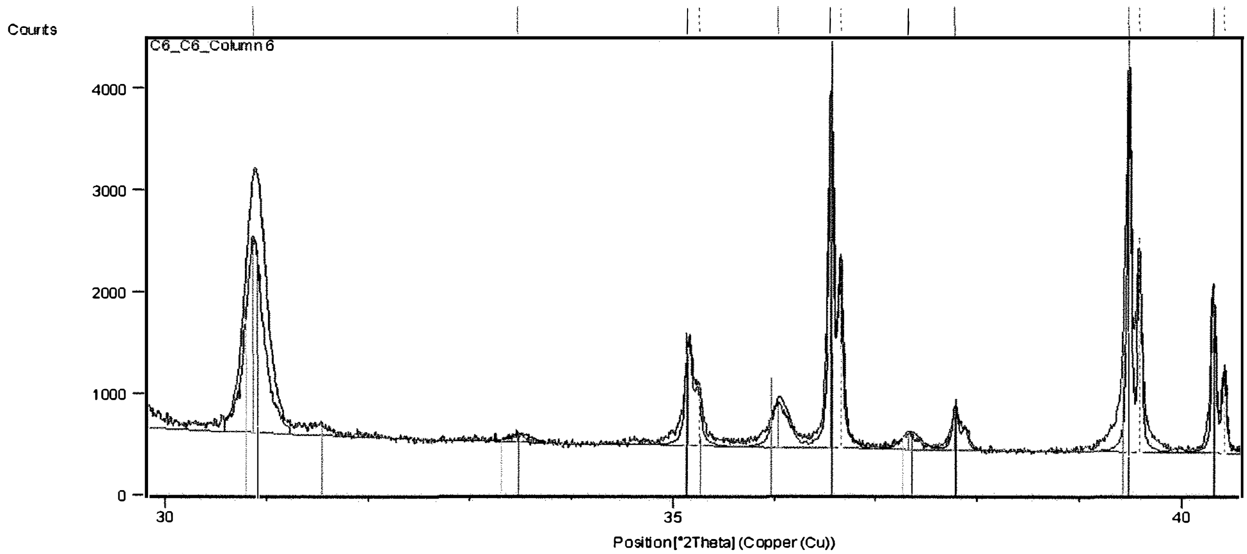
(a) X-ray diffraction pattern for flow-through reactor 6 (8 – 90 °2-theta).



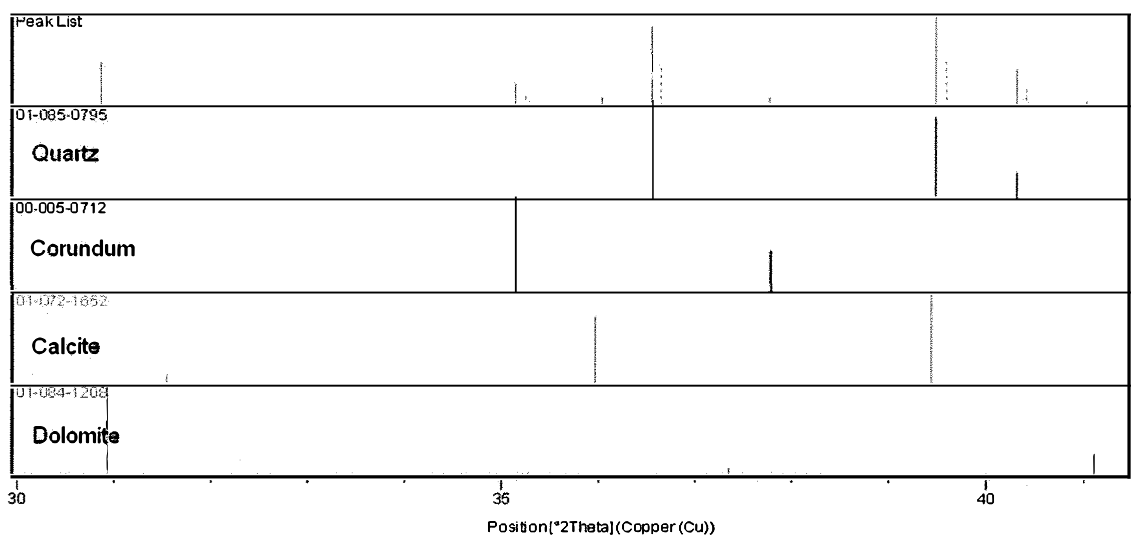
(b) ICDD PDF-2 database peak matches for flow-through reactor 6.



(c) Expanded view 30 to 41 °2-theta, showing key x-ray diffraction peaks for reactor 6.

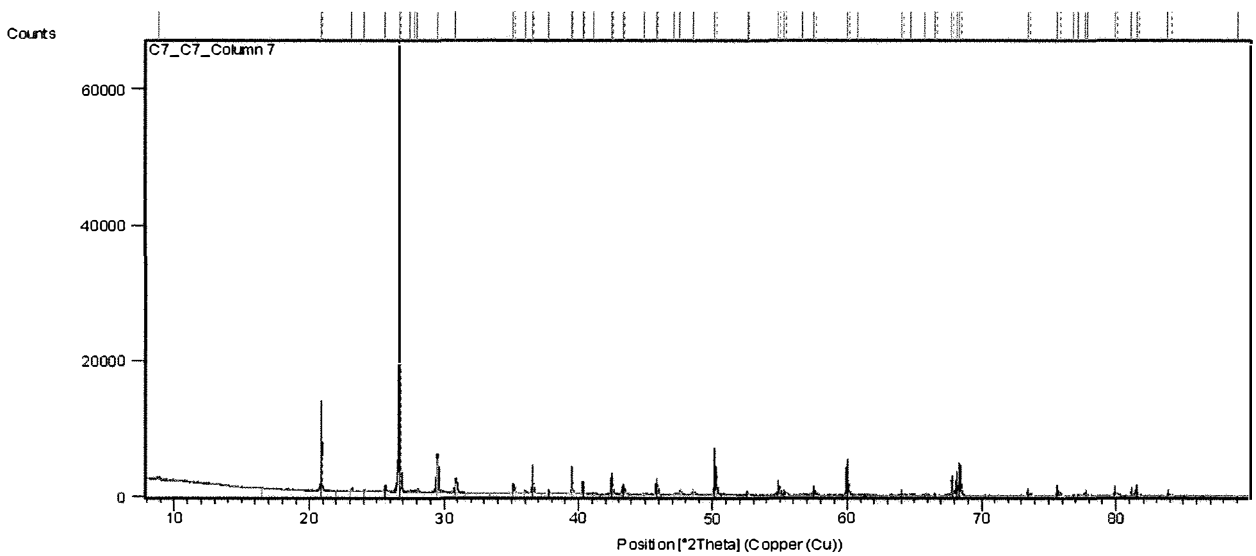


(d) Expanded view 30 to 41 °2-theta, showing ICDD PDF-2 database peak matches for reactor 6.

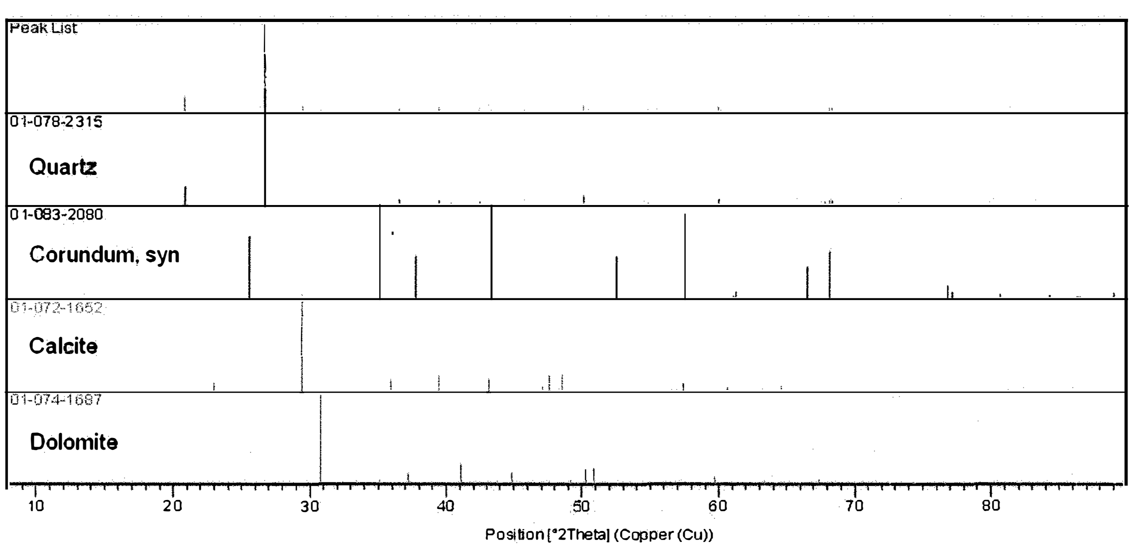


Flow-through Reactor 7

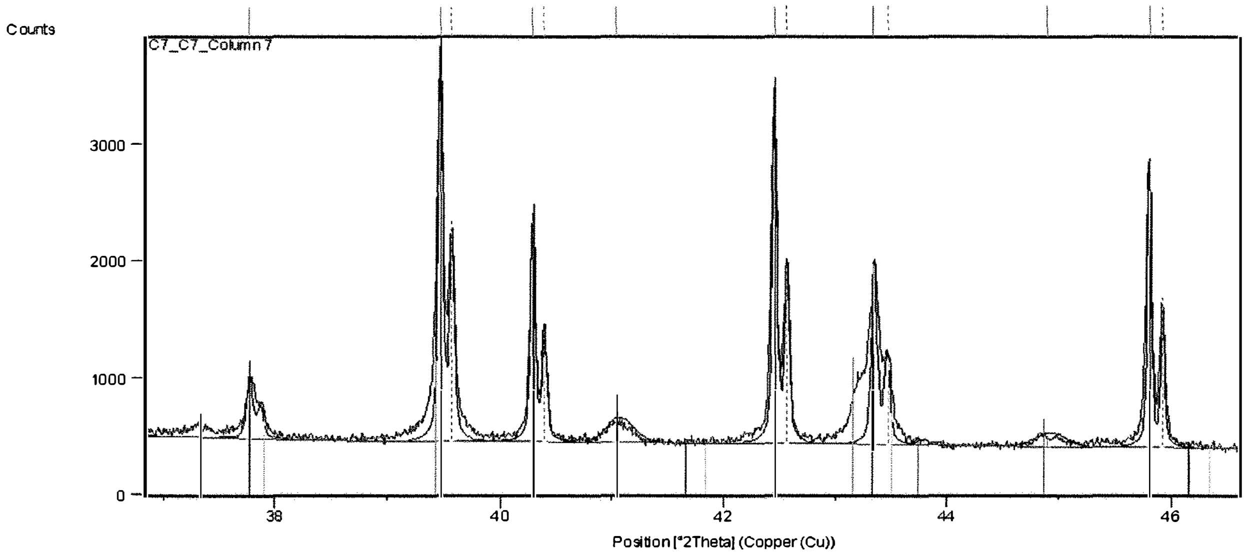
(a) X-ray diffraction pattern for flow-through reactor 7 (8 – 90 °2-theta).



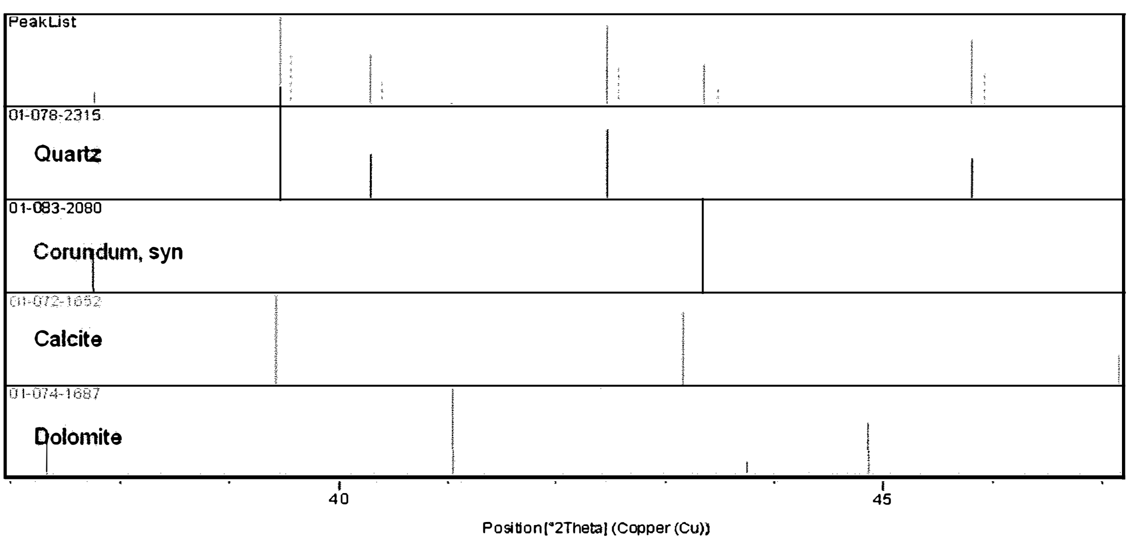
(b) ICDD PDF-2 database peak matches for flow-through reactor 7.



(c) Expanded view 37 to 47 °2-theta, showing key x-ray diffraction peaks for reactor 7.

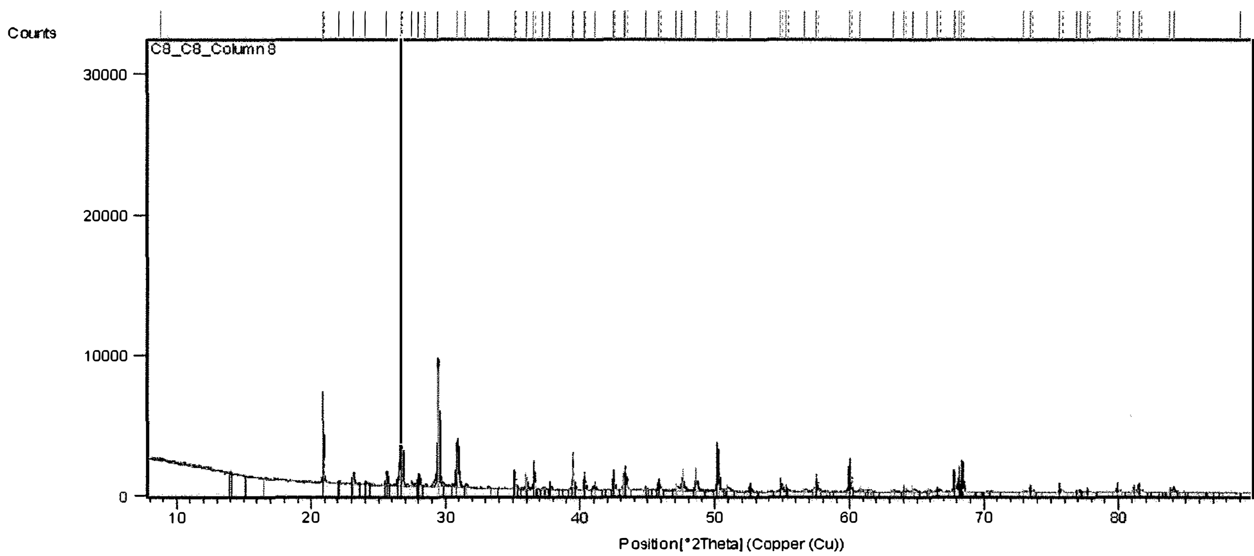


(d) Expanded view 37 to 47 °2-theta, showing ICDD PDF-2 database peak matches for reactor 7.

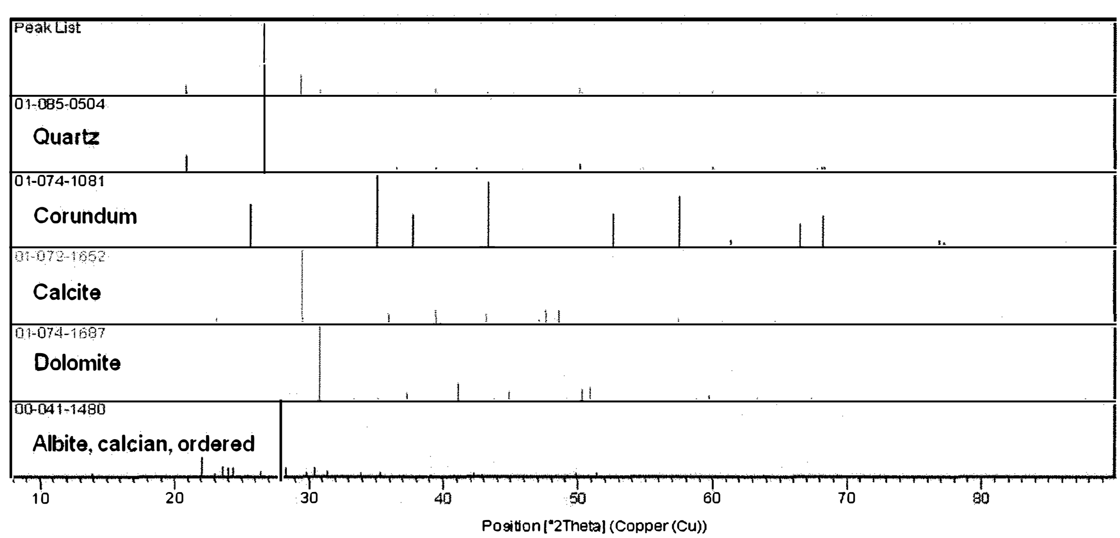


Flow-through Reactor 8

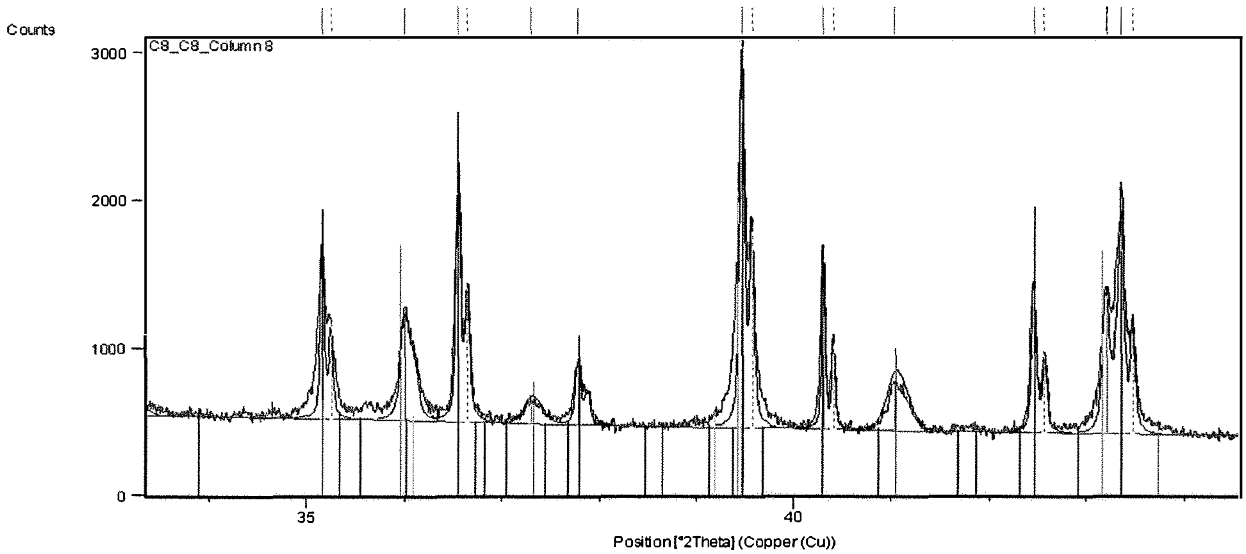
(a) X-ray diffraction pattern for flow-through reactor 8 (8 – 90 ^{o}2-theta).



(b) ICDD PDF-2 database peak matches for flow-through reactor 8.



(c) Expanded view 33 to 45 °2-theta, showing key x-ray diffraction peaks for reactor 8.



(d) Expanded view 33 to 45 °2-theta, showing ICDD PDF-2 database peak matches for reactor 8.